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UPLIFT PRESSURE AND DESIGN OF WEIRS WITH TWO SHEET PILES.

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Received June 19, 1936.

In a series of papers published in these *Proceedings* and in the *Memoirs of the Irrigation Research Institute*, investigations on the effect of single sheet piles on the uplift pressure on floors have been reported. In the present paper, the results of an investigation on the effect of two sheet piles on the uplift pressure are given. The latter is more important from a practical standpoint, as it is now recognised that a downstream pile is essential for controlling the exit gradient and that an upstream sheet pile affords protection against scour upstream. In larger works, three and even four sheet piles are present ; as for example, three sheet piles are proposed for the Trimmu Weir in the Punjab and four piles have been put in, under the floor in the Sukkur Barrage. Investigations on three sheet piles will be reported in a subsequent paper.

While a theoretical solution exists for the case of a single sheet pile under a flush floor, no theory has so far been developed for the case of two sheet piles. At present an experimental solution of the two sheet pile case is the only one possible. The present investigation aims at obtaining working rules for purposes of design for most of the ordinary cases of weirs with two sheet piles.

It has already been established in previous publications,[1,2] that the hydraulic and the electrical potential methods of investigating the uplift pressures under weirs lead to identical results. The problem of examining various models has thus been very much simplified by employing the electrical method.

In the present investigation three series of experiments with two sheet piles were carried out. These were :—

1. Two sheet piles of equal length at heel and toe.
2. Two sheet piles of different lengths at heel and toe.
3. Two sheet piles of equal length not at heel and toe.

The values of the ratio of the length of the piles to that of the floor are generally kept within the range, which occurs in practice.

*Results.**

1. Sheet Piles of Equal Lengths at the Heel and Toe.—In this series of experiments, the model had a 12″ floor with sheet piles of 0·0″, 0·5″, 1·0″, 1·5″, 2·0″, 3·0″ and 4·0″ each, fixed one at the heel and the other at the toe. Since the heel and the toe sheet piles are of equal length, the pressure distribution is symmetrical with respect to the centre of the floor and, therefore, only results on one-half of the floor are shown. The curves A_0 to A_6 in Fig. 1 show the uplift pressure beneath the floor in each case. The ordinate in the figure shows the percentage pressures and the abscissa, the length along the floor and each face of the sheet pile. The length of the pile in each experiment is marked on the curves and the position of the points B and C are shown in the inset.

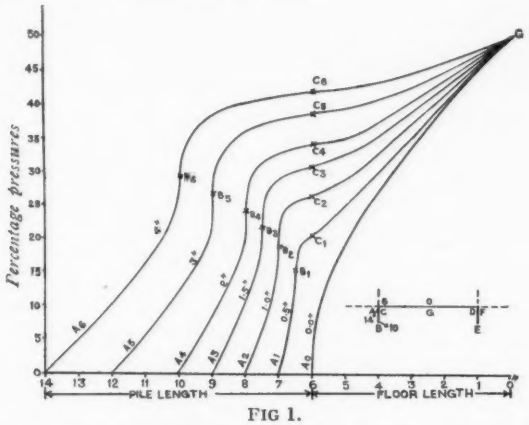

FIG 1.

Hydraulic Gradients—Sheet Piles of Equal Length at Heel and Toe.

An examination of any of these curves reveals many points of application for purposes of design. Fig. 2 shows the uplift pressure at the points B and C for different values of α, the ratio of the length of a pile to that of the floor. Take for example the curve A_2 in Fig. 1. This curve shows the uplift pressure for the case of a 1″ sheet pile with a 12″ floor, or a value of α equal to 1/12. Referring to Fig. 2, it will be seen that the uplift pressures at the points B and C for this value of α are 19 and 26·5 per cent. respectively. Similarly when measured from the upstream side the pressures at the points D and E are 73·5 and 81 per cent. respectively. The floor at the point D should, therefore, be designed so thick as to withstand this uplift pressure

* Since the law of similarity holds good in these investigations, the results of the model apply to a prototype projected to any scale.

of 73·5 per cent. of the head and that at B, to withstand 26·5 per cent. of the head. If, for example, a 15 ft. head is the maximum that is likely to act from the upstream side, the floor at D should be 7·9 ft. thick and that

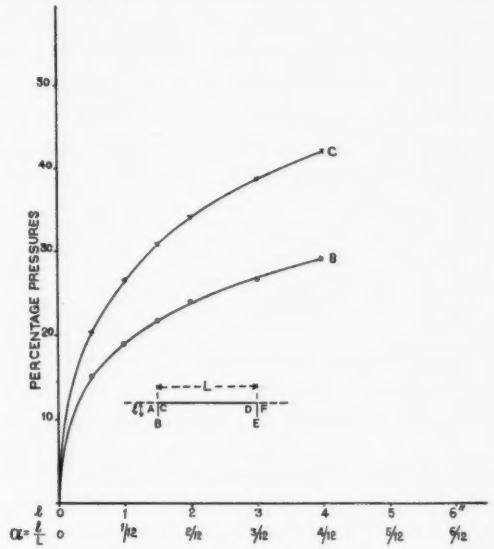

FIG. 2.
Pressures at B and C.

at B should be 2·8 ft. thick. As could be seen from the curve, the pressure gradient on the floor is not quite uniform between the piles. But the deviation from uniformity is small and not such as to be taken into account in practice. The thickness of the floor can, therefore, be uniformly decreased from 7·9 to 2·8 ft. If further accuracy in designing the thickness is desired, a point to point calculation can be made from the curve in Fig. 1. Similar calculations can easily be made for the case of weirs having other values of α.

It may be pointed out that this calculation is made for the static head acting from the upstream side. When there is flow over the weir or when there is water always standing on the downstream floor, these conditions may modify the thickness. The uplift pressure will also be considerably influenced by the silt upstream. But these conditions are such as to tend to reduce the uplift pressure and hence when once the weir has been designed for the static head, it has been done for the worst condition likely to occur. If, however, a scour occurs on the upstream, the condition is not safe, as that will tend to increase the uplift pressure. A scour should not, therefore,

be allowed to occur or extra provision should be made against this cause in the design.

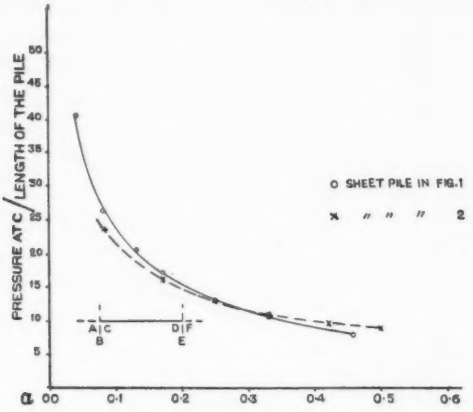

FIG. 3.

Efficiency of Sheet Pile with Respect to its Length.

Another point of great importance is the effect of the length of the sheet pile and its efficiency with regard to pressure reduction. It has already been observed in the investigation of one sheet pile and also it follows from the theory of that, that the rate at which unit length of a pile cuts off the pressure, decreases rapidly when the length of the pile is increased. The case of two sheet piles is also similar. The continuous line in Fig. 3 shows the pressure cut off by piles of various lengths. The ordinate in Fig. 3 represents the quantity, pressure cut off divided by the length of the pile, and the abscissa the corresponding lengths of the pile. The quantity represented by the ordinate is termed relative efficiency with respect to the length of the piles. It will be seen that the curve tends to become asymptotic to the abscissa, indicating that the longer the pile, the less efficient it becomes per unit length. Thus, referring again to Fig. 3, the average pressures cut off by the pile per unit length for values of α equal to 0·1 and 0·2 are 23·5 and 15·5 respectively. Thus in the latter case, a pile twice that of the former one will reduce the pressure only by 31 per cent. and not by 47 per cent., as would be expected if it followed a linear law.

2. *Sheet Piles at Heel and Toe but of Unequal Lengths.*—Unlike the case discussed above, in the construction of many weirs, the toe and the heel piles are of different lengths. In the series of experiments now to be mentioned, the length of the pile at the heel was kept constant at 3″ and

the floor at 12″. The pile at the toe was increased from 0 to 6″ by increments of 1″. Since the pressure distributions are reversible, the cases of the heel and toe piles are also reversible. The uplift pressure under the floor is shown in curves A_0 to A_6 in Fig. 4; the lengths of the piles being indicated by the suffixes to A in the figure. The ratio of the length of the pile at the toe to that of the floor in these cases is termed α_1. For the sake of convenience in plotting, the centre of the floor is taken as the origin. Since the case is not symmetrical, the pressure gradients under the entire length of the floor are plotted. In other respects the curves are to be interpreted similarly to those in Fig. 1 and the calculations for purposes of design to be made in the same manner.

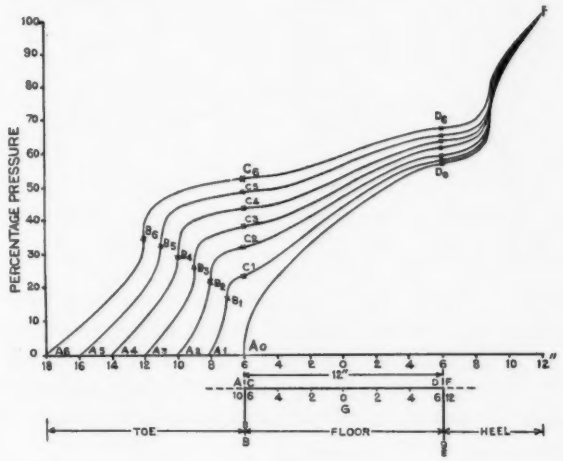

FIG. 4.

Hydraulic Gradients—Sheet Piles at the Toe Varying.

Fig. 5 shows the pressure at the points B and C at the toe corresponding to those of Fig. 2 in the symmetrical case. The dotted line in Fig. 3 shows the relative efficiency per unit length of the pile at the toe and is to be interpreted similar to that of the continuous line in the same figure. The fact that the two curves run near each other indicates that unless the ratio α and α_1 are widely different, the laws of variation of efficiency are similar.

Another important point that may be emphasised with reference to Fig. 4 is that when α_1 changes from 0 to 0·5 and the pressures at the point C vary from 0 to 53 per cent., the corresponding change at the corner D of the pile (Fig. 4) at the heel is only 10 per cent. α_1 is generally much smaller than 0·5 in practice, and hence the effect on the uplift pressure

at the upstream corner of the floor caused by a change in length of the downstream pile can be considered in most cases as negligible. This fact

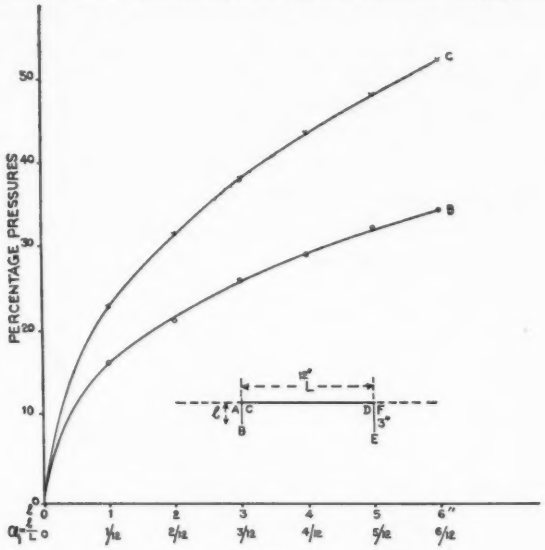

FIG. 5.

Pressures at B and C—Sheet Piles at Heel and Toe of Different Lengths.

makes it possible to obtain approximate values of the pressure, by applying the analysis of a single sheet pile case, to that of two sheet piles. This method is very approximate and can only be recommended, when there is no other method at the disposal of the designing engineer. It may lead to errors of the order of 10 per cent.

The best method is to subject the design to an experimental test or in the absence of that, to obtain a graphical solution from the curves given in this investigation. A method of design, employing the graphical solutions obtained in the present investigation, is given in a subsequent section.

3. Two Sheet Piles of Equal Lengths not at the Heel and Toe.—In both the series of experiments mentioned in the foregoing sections, the sheet piles were at the heel and toe. In actual works, there are frequently impervious aprons projecting beyond the upstream and the downstream piles. In the series of experiments now to be discussed, two sheet piles each of one inch length were associated with a floor 12″ long. The distance between the piles was maintained at 6″ and the piles moved so that the distances of the downstream pile from the toe were 0, $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$ and 3 inches in each experiment. The pressure distributions under the floor are shown in curves A_1 to A_6 respectively in Fig. 6. The scales along the ordinate

are displaced for the sake of economising space. The positions of the points are indicated in the inset. The curves of Fig. 6 can again be employed for purposes of design as indicated in Section 1.

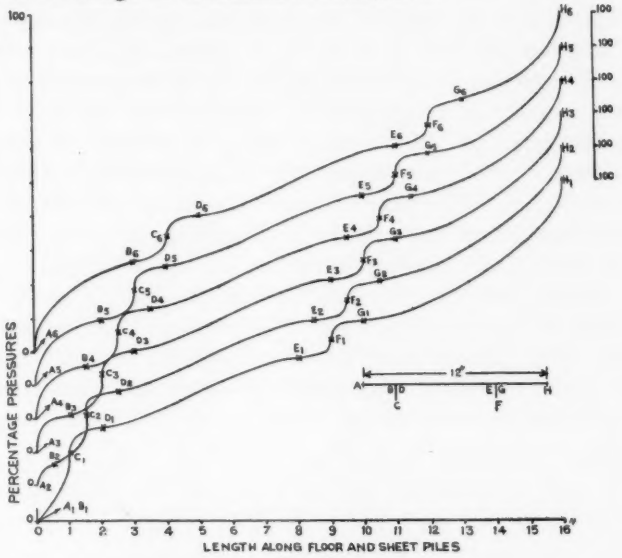

FIG. 6.
Sheet Piles of Equal Length not at Heel and Toe.

The most important point that emerges from this series of experiments is the efficiency of a pile with respect to its position under the floor. This question is of very great importance and the answer is given in Fig. 7. As

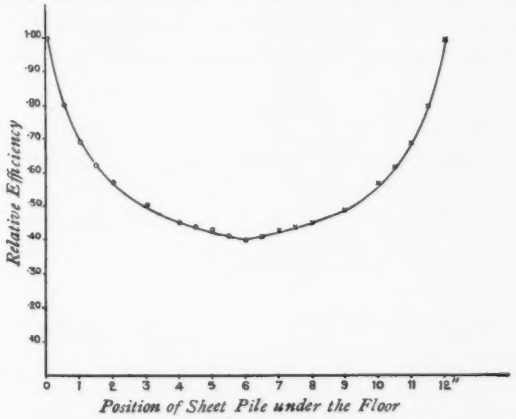

FIG. 7.
Efficiency of a Pile at the Toe compared with its Efficiency at any Position under the Floor.

has already been shown in the discussions relating to a single sheet pile,[3,4] a pile is found to be the most effective in reducing pressure, when it is situated at the toe or at the heel. The case is also similar in the case of two sheet piles. In the figure, the abscissa represents the position of the pile under the floor, and the ordinate a term called relative efficiency. The latter term gives the pressure cut off by a pile at any position compared to that cut off by the same pile taken as unity, when it is at the toe. It can be seen from the figure, that if a certain length of a sheet pile cuts off unit pressure when it is at the toe or heel, the same pile when removed to one-fourth of the distance of the floor towards the centre will cut off only half the pressure which it did previously. If it is removed to the centre it will cut off only 0·4. This shows again that in the two-sheet pile case as well, the best position of a pile is towards the heel or toe. This investigation has only been carried out for a value of 1/12 for α. This value of α is frequently adopted in practice and for other values of α near 1/12, the change in relative efficiency will be very small and hence the same curve can be employed for most of the practical cases.

4. Graphical Solution for a General Design.—The graphical results obtained in this investigation can be employed for purposes of general design of weirs with two sheet piles. To illustrate this, consider the following example. It is required to design a weir to withstand the uplift pressure under the following conditions : (i) The total length of the floor is 150 ft., (ii) it is to have two sheet piles one being 50 ft. downstream of the heel and the other at the toe, (iii) the head for which it is to be designed is 20 ft., static head.

The first point to be considered in the design is the control of the exit gradient below the point C (Fig. 8) on the downstream side. It has been

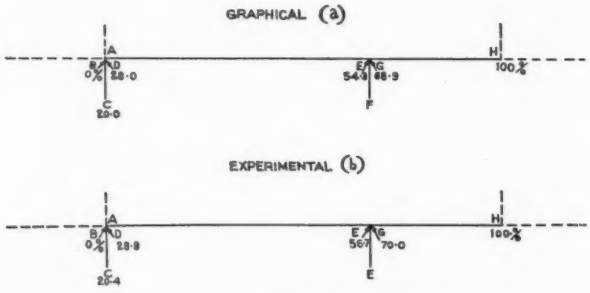

FIG. 8.

Comparison of Graphical and Experimental Solutions.

accepted that an average exit gradient of 1 : 4 beyond the point C is safe at the toe end. Now referring to Fig. 2, it is found that 20 per cent. of the head will be left at the point C for a value of α equal to 0·1. This leaves 4 ft. of head at the point C for a 15 feet pile, being about the safe limit for the length of the pile, from the point of view of the exit gradient. The pressure at the point D (Fig. 8) for this length of the pile is 28 per cent. as can again be obtained from Fig. 2. The next point to decide is the pressure cut off by the upstream pile. If a 15 ft. pile is also to be placed at 50 ft. towards the downstream of the heel, the pressure which this pile cuts off will be found to be 14·6 per cent.* It follows that the pressure now remaining to be carried by the floor is 57·4 per cent. The next point is to determine the distribution of the 57·4 per cent. of this pressure on the floor between the piles and upstream of the intermediate pile. Referring to curve 5 in Fig. 6 the clue to this distribution can be obtained. Curve 5 represents a case nearest to the one which is intended to be designed. It will be seen from the series of curves in Fig. 5, that altering the position of the piles under the floor does not change the *nature* of the distribution between them to any considerable extent. Hence the pressures can be taken to be proportional to the length of the floor between the pile. Curve 5 shows that 20·3 per cent. of the pressure is cut off by the floor between the piles and 32 per cent. by the floor above the intermediate pile. In the new design, the length of the floor between the piles is increased in the ratio 100 : 75, the other part of the floor remaining the same. Hence the ratio of the pressures which will be borne by the respective portions of the floor is $20{\cdot}3 \times 100/75 : 32$ (*i.e.*) 27 : 32. Dividing 57·4 per cent. in this ratio, 26·3 and 31·1 per cent. are obtained as the pressures to be borne by the portions DE and GH of the floor (Fig. 8) in the weir under design. Thus the pressures at the important points of the weir, to be designed, are obtained. These are marked in Fig. 8 (*a*).

With a view of checking the accuracy of the graphical solution, a model of the design was tested experimentally and the pressures thus obtained are given in Fig. 8 (*b*). On comparing the two figures, it will be seen that the maximum difference obtained by the two methods is 2·5 per cent. at the point E. This difference is not serious in practice.

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* This can be obtained as follows:—

Referring to Fig. 3, it may be found that for a ratio of α equal to 1/12 the efficiency of the pile is 26.5. Referring to Fig. 7, the efficiency due to its present position is .46. The actual value of α in the new design is 1/10. Hence, the pressure that this pile will cut off is $26{\cdot}5 \times 12/10 \times {\cdot}46 = 14{\cdot}6$ per cent.

Summary.

Models of weirs with two sheet piles have been investigated for the pressure distribution. Three series of experiments were carried out. In the first series the sheet piles were of equal length at the heel and toe ; in the second series, they were of unequal lengths but again situated at the heel and toe ; and in the third series, the piles were of equal length but not at the heel and toe. The results obtained are represented graphically in Figs. 1 to 8. The efficiencies of the sheet piles, with respect to their position under the floor and with respect to their length, have been examined.

Employing the graphical results obtained in the investigation, a method of obtaining the uplift pressures for a new design has been illustrated. The results of the graphical solution thus obtained were tested experimentally. The results by the two methods are found to agree giving a maximum difference of only 2·5 per cent. for the uplift pressure and this not at an important point. Attention has also been drawn to the fact that as the toe of a weir is its vulnerable point, weir design must commence from the downstream end, so as to control the exit gradient.

In conclusion we have great pleasure in thanking Dr. E. McKenzie Taylor, the Director, for his keen interest in the problem.

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4. W. Weaver, *Journal of Mathematics and Physics*, 1932, **11**, 114.

GEOMETRICAL INVERSION IN THE ACIDS DERIVED FROM THE COUMARINS.

Part III. *Trans* to *Cis*.

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Received June 8, 1936.

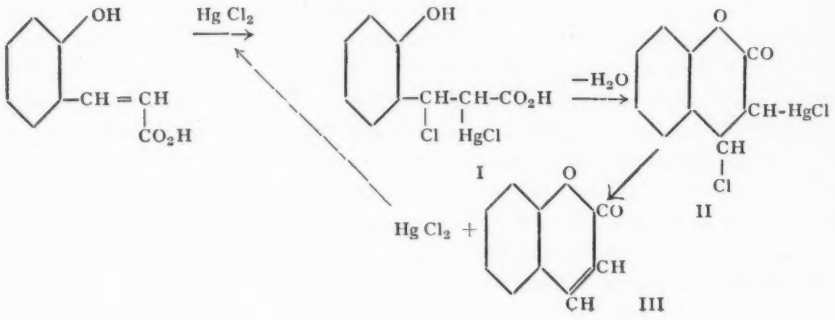
In Part I[1] it was shown that coumaric acids (*trans*) as a rule decompose when heated above their melting points into carbon-dioxide and hydroxy-styrenes whereas the corresponding esters undergo conversion into the coumarins with the evolution of alcohols.

In the course of our investigation of certain mercurated coumaric acids we noticed that their decomposition was rather abnormal since only a fraction of the expected quantity of carbon-dioxide was evolved. We were consequently led to examine the decomposition of coumaric acids in the presence of added mercury compounds and we found that in the presence of mercuric oxide the decomposition of the acids took place much below their melting points and from the products over 50% yield of the pure coumarins could be isolated. The conditions of the decomposition seem to indicate that due to the influence of the mercury compound on the double bond inversion of the *trans* acid to the *cis* form first takes place with the subsequent ready elimination of water at a comparatively low temperature.

Amongst the methods of producing *trans* to *cis* inversion concentrated sulphuric acid at 100° has been sometimes used. But no details about the scope of this method are available in the literature. On careful examination it is now found that this method gives only a poor yield of coumarin and 7-methylcoumarin (10–15%) from coumaric and 4-methylcoumaric acids respectively. About 5% only of the original acids could be recovered after the reaction. The loss of the remaining portion may be due to simultaneous nuclear sulphonation taking place resulting in the formation of soluble sulphonic acids. From 5-nitrocoumaric acid, however, an almost theoretical yield of 6-nitrocoumarin was produced. This could be attributed to the influence of the nitro group on one or both of the following factors, (1) the facility with which inversion takes place and (2) the hindrance to nuclear sulphonation.

When boiled with an alcoholic solution of 2% hydrogen chloride, coumaric acid gives a good yield of the ester whereas with a higher concentration of hydrogen chloride coumarin formation takes place.[1] It is now found that if alcohol saturated with hydrogen chloride is employed about 75% yield of coumarin is obtained from coumaric acid and about 30% yield of 7-methylcoumarin from 4-methylcoumaric acid. Obviously, this reagent is superior to sulphuric acid for these two cases. No ester could be isolated probably due to its immediate conversion into coumarin. On the other hand, 5-nitrocoumaric acid gave about 20% yield of the ester and no nitrocoumarin could be obtained. For this case sulphuric acid is the better reagent.

The most satisfactory method of producing this *trans* to *cis* inversion is by the use of mercuric chloride. When this substance is mixed with coumaric acid and the mixture is very carefully heated to the melting point of the acid coumarin is produced and can be isolated. But the conditions are very difficult to control and further change to a dark tarry mass takes place rapidly. No enhanced yield is produced when it is employed in conjunction with concentrated sulphuric acid or alcohol saturated with hydrogen chloride. When the *trans* acids are boiled with dilute aqueous hydrochloric acid containing mercuric chloride the conversion into the coumarins was not satisfactory. The easiest method is to boil the *trans* acids with water containing mercuric chloride. Coumaric acid gave a theoretical yield of coumarin mercuric chloride addition product on boiling equimolecular quantities of the two with water.[2] This addition product is easily decomposed with very dilute hydrochloric acid to yield coumarin. As shown in the experimental section a small quantity of mercuric chloride is enough to effect transformation of large quantities of the *trans* acids and almost theoretical yields of coumarin, 7-methyl and 6-nitrocoumarins are obtained. Mercuric chloride seems to function in virtue of its capacity to add on to the double bond. The following mechanism is suggested as the most probable.



Coumarin mercuric chloride (II) which could be isolated as an intermediate product is obviously capable of undergoing sufficient dissociation in solution to make the transformation complete (*compare* Clayton,[2] *loc. cit.*).

The use of sun light as a convenient method for effecting *trans* to *cis* inversion has been described in Part I. Regarding the use of sodium sulphite for this purpose reference should be made to the work of Dodge[3] and Dey and Row.[4] Its addition to the *trans* acid seems to be slow though the subsequent conversion into coumarin may be easy.

Experimental.

Action of heat and mercuric oxide.—Coumaric acid (5 g.) was intimately mixed with mercuric oxide (1 g.) and heated in a tall pyrex test-tube of large capacity by means of an oil bath. Decomposition set in even at 170° and was completed by gradually raising the temperature to 210° which is the melting point of free coumaric acid. The mixture was occasionally stirred with a glass rod in order to facilitate the decomposition. Some coumarin sublimed on to the upper portions of the boiling tube. After cooling, the mixture was ether extracted, the extract shaken with 1% sodium hydroxide in order to remove impurities, washed again with water and finally evaporated. Pure coumarin was produced melting at 68–69°, the yield being about 50%.

4-Methylcoumaric acid behaved quite similar to coumaric acid and gave about the same yield of 7-methylcoumarin melting at 126–127°. The decomposition began even at about 150° and was completed by raising the temperature to 200°. In the case of 5-nitrocoumaric acid a similar yield of 6-nitrocoumarin was obtained. After completing the decomposition, the product was extracted with alcohol, the solution distilled to remove alcohol, the resulting solid triturated with cold aqueous sodium bicarbonate and filtered. The residue was pure 6-nitrocoumarin melting at 187–188°.

Action of concentrated sulphuric acid.—Coumaric acid (2 g.) was treated with concentrated sulphuric acid (15 c.c.) and the solution heated at 100° (water-bath) for 2 hours. After cooling it was poured into water, the mixture ether extracted, the ether extract shaken with aqueous sodium carbonate in order to remove unchanged acid and after drying evaporated in a tared flask. The product was pure coumarin, the yield being about 10%. On acidifying the sodium carbonate extract and extracting with ether, about 5% of the coumaric acid that was taken was recovered. The yield of coumarin was less when the duration of heating was altered.

4-Methylcoumaric acid was studied in an identical manner and it gave a similar yield of 7-methylcoumarin. In the case of 5-nitrocoumaric acid,

after heating the mixture with sulphuric acid it was poured into water, the precipitate filtered, washed with water, triturated with aqueous sodium bicarbonate, filtered and washed. The residue was found to be pure 6-nitrocoumarin. The yield was 95% in 4 hours, 80% in 2 hours and 60% in 1 hour.

Action of alcoholic hydrogen chloride.—Coumaric acid (2 g.) was dissolved in absolute alcohol (25 c.c.) and the solution saturated with hydrogen chloride in the cold. It was left overnight and next morning boiled under reflux for 2 hours. It was then distilled to remove most of the alcohol, water was then added, the whole extracted with ether and the ether solution shaken up with aqueous sodium carbonate. After drying over calcium chloride the ether solution was evaporated in a tared flask. The residue was pure coumarin, yield being 75%. Balance of the unchanged acid was recovered from the sodium carbonate solution.

4-Methylcoumaric acid gave 30% yield of 7-methylcoumarin under the same conditions. In the case of 5-nitrocoumaric acid instead of ether extracting the product, it was filtered, washed with water, triturated with sodium bicarbonate solution, filtered and washed with water. The residue (yield 25%) was almost completely soluble in 1% sodium hydroxide and after one crystallisation from alcohol was found to melt at 171°. Mixed melting point with ethyl 5-nitrocoumarate was the same. From the sodium bicarbonate extract almost all the unreacted acid was recovered.

Action of mercuric chloride.—(1) Coumaric acid (1 g.) was intimately mixed with mercuric chloride (2 g.) in a test-tube and slowly heated up in an oil bath. At about 190° decomposition started. The temperature was kept steady at this and the mixture stirred. With further rise of temperature it turned brown and underwent complicated changes. About two minutes were found to be the optimum for heating. The product was repeatedly extracted with small quantities of boiling water. The residue was a resin insoluble in water, alcohol and ether. The aqueous solution deposited a colourless crystalline solid on cooling. The whole was shaken up with a fairly large volume of ether, ether solution extracted with aqueous sodium bicarbonate in order to remove a small quantity of unchanged coumaric acid and ether evaporated. A colourless crystalline solid melting at 165° and identical with coumarin mercuric chloride was obtained (yield 0·5 g.). When boiled with 3% hydrochloric acid for 5 minutes it gave coumarin.

(2) Finely powdered coumaric acid (1 g.) and mercuric chloride (2 g.) were boiled with water (100 c.c.) for two hours. On cooling the clear solution, colourless needles of coumarin mercuric chloride, melting at 165°,

were formed. The solid was filtered and the mother-liquor extracted with ether when some more of it was obtained. The yield was theoretical.

(3) Coumaric acid (1 g.) was treated with water (25 c.c.) and a small quantity of mercuric chloride (0·1 g.) and boiled under reflux for 2 hours. At first the mixture was turbid and in about 15 minutes the solution became clear with some viscous liquid (coumarin) floating about. At the end of 2 hours concentrated hydrochloric acid (1 c.c.) was added to the boiling liquid and then allowed to cool. The viscous liquid solidified to a crystalline solid and more crystals were deposited on cooling the solution. After filtering, an almost theoretical yield of pure coumarin (m.p. 68°) was obtained. A very small quantity of it was recovered from the aqueous solution by ether extracting. It should be noted that if hydrochloric acid was added at the beginning of the heating, very little coumarin was produced.

(4) 4-Methylcoumaric acid under exactly the same conditions as above gave an almost theoretical yield of 7-methylcoumarin. 5-Nitrocoumaric acid required longer heating and more mercuric chloride for producing a good yield of 6-nitrocoumarin. The acid (1 g.) was mixed with mercuric chloride (0·5 g.) and water (50 c.c.) and boiled for 6 hours. Concentrated hydrochloric acid (2 c.c.) was then added and allowed to cool. The crystalline product melted at 185–187° with a little previous sintering. When triturated with a little cold sodium bicarbonate solution, filtered and washed, a very small quantity of unchanged acid was removed and the product melted sharp (187–188°), and was found to be identical with 6-nitrocoumarin, yield being over 90%.

Summary.

Coumaric acids which ordinarily form hydroxystyrenes on heating yield the corresponding coumarins when heated in the presence of mercuric oxide or chloride. The scope of the use of concentrated sulphuric acid and alcohol saturated with hydrogen chloride for producing *trans* to *cis* inversion has been examined. The former is useful for nitrocoumaric acid whereas the latter is suitable for coumaric and methylcoumaric acids. Mercuric chloride in neutral aqueous solution has been found to be very satisfactory for both types of acids.

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REACTIVITY OF THE DOUBLE BOND IN COUMARINS AND RELATED α-β UNSATURATED CARBONYL COMPOUNDS.

Part II.* Reaction of Mercury Salts on Coumarins.

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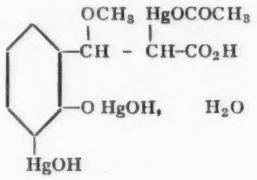
That the double bond in coumarins is reactive has been established from the easy addition of typical reagents. Clayton[3] was the first to prepare coumarin compounds containing mercury. He found that coumarin and alkyl substituted coumarins combine with an equimolecular proportion of mercuric chloride readily in the cold to form addition products and he was of the opinion that the mercuric salt was held by the oxygen of the pyrone ring by means of residual affinity. Biilmann[2] could observe no reaction between coumarin and mercuric acetate in methyl alcoholic solution and was led to think that it did not contain an ordinary ethylenic link, since derivatives of coumarinic and coumaric acids reacted readily in the cold, the double bond being the point of attack by the reagent. Sen and Chakravarti[9] remarked that mercuric chloride and mercuric acetate failed to mercurate coumarin in aqueous, alcoholic or acetic acid solution. Therefore, they opened up the pyrone ring by dissolving the coumarins in aqueous alkali and subsequently effected mercuration of the coumarinic acids and their salts either by treatment with mercuric acetate in cold aqueous solution or by boiling with yellow mercuric oxide (see Naik and Patel[8]). With a group of coumarins as represented by 6-nitro and 6 : 8-dibromocoumarin they noticed that inversion to the coumaric acid took place and no mercuration was effected. With another group as typified by 7-hydroxy-4-methylcoumarin they found that mercuration of the benzene ring took place whereas no inversion was produced. That coumarin itself under these conditions gives coumaric and mercurated coumaric acids has been recently shown by us.[11] Recently after our work described in this paper had made considerable

* Part I appeared in *J. C. S.*, 1928, 166.

progress, a paper by K. Matejka[6] on the mercuration of cinnamic acid, safrole and coumarin appeared. This author observed mercuration of coumarin in hot alcoholic solution using mercuric acetate and claimed to have isolated two compounds of the following probable formulæ. But these rather unusual constitutions are based only on the analysis for carbon, hydrogen and mercury of specimens which were probably not pure and not on an adequate study of their properties or the preparation of known derivatives.



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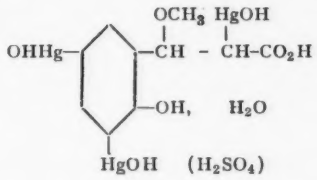
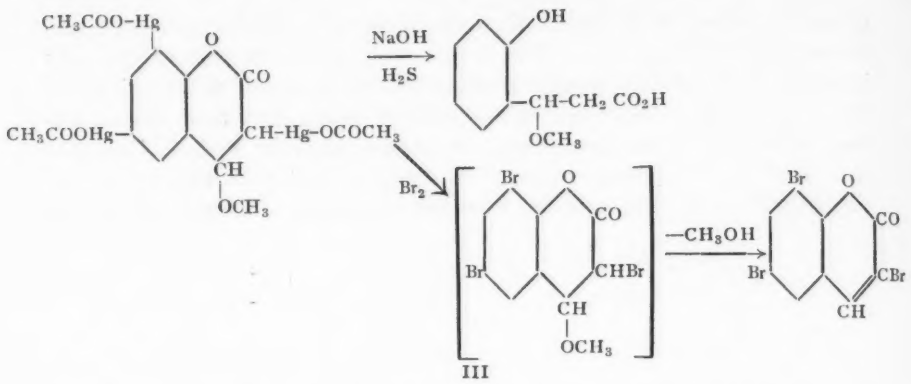


II

Contrary to previous statements it is now found that coumarin reacts slowly in the cold with mercuric acetate in methyl alcoholic solution yielding a trimercury compound. The reaction is less slow when the solution is boiled. Irrespective of the molecular proportions 1, 2 or 3 of mercuric acetate employed the same product, 3 : 6 : 8-triacetoxymercuri-4-methoxymelilotic anhydride is obtained. Though with the larger proportions the yield improves, purity suffers due to admixture with an impurity containing a higher percentage of mercury and a lower percentage of carbon, which is probably mercurous acetate. The substance cannot be crystallised from any of the ordinary organic solvents since it is sparingly soluble. It is insoluble in sodium carbonate, but dissolves in aqueous ammonia and sodium hydroxide easily in the cold and on passing hydrogen sulphide into these solutions all acetoxymercury groups are replaced by hydrogen atoms, the resulting product being β-methoxymelilotic acid (Biilmann, *loc. cit.*). The mercury compound reacts rapidly with bromine in the cold in the presence of glacial acetic acid producing mercuric bromide and 3 : 6 : 8-tribromocoumarin which is identified by comparison with an authentic specimen (Simonis and Wenzel, 1906) and by conversion into 4 : 6-dibromocoumarilic acid. From these the constitution of the mercury compound is clearly established as III and hence it has to be concluded that mercuric acetate reacts with the double bond in coumarin and also mercurates the benzene ring in 6 and 8 positions.

7-Methylcoumarin behaves similar to coumarin though the reaction with mercuric acetate is slower still. By the action of aqueous alkali and



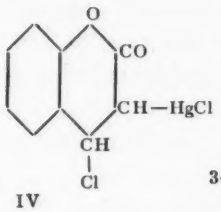
hydrogen sulphide on the trimercury compound 4-methyl-β-methoxymelilotic acid could not be isolated probably due to its instability, 4-methylcoumaric acid being obtained instead. The formation of a coumaric acid under these conditions seems to take place only when the double bond originally has been attacked by the mercuric salt. On treatment with bromine it gives a tribromo-7-methylcoumarin which from analogy is considered to be 3 : 6 : 8-tribromo-7-methylcoumarin.

6-Nitrocoumarin forms a dimercury compound which is 6-nitro-3 : 8-diacetoxymercuri-4-methoxymelilotic anhydride. With aqueous alkali and hydrogen sulphide it gives 5-nitrocoumaric acid and with bromine 3 : 8-dibromo-6-nitrocoumarin which is found to be identical with that of Dey and Row.[4] Hence with 6-nitrocoumarin besides addition at the double bond mercuration in the 8 position takes place.

Though it is now established that mercuric acetate is capable of reacting with the double bond in coumarin it has to be accepted that the reactivity is far less than in the case of coumaric and cinnamic acids and similar compounds. Just the opposite was experienced with cyanacetamide and sodium sulphite.[10] This reversal in the order of reactivity seems obviously to be due to the differences in the nature of the reagents employed, and the remarks made in Part I on the influences controlling the reactivity of the double bond in coumarins seem to hold good.

The reaction of mercuric chloride on the three coumarins mentioned above and the products obtained therefrom have now been more closely studied. Coumarin and 7-methylcoumarin react readily in the cold in the presence of any of the ordinary organic solvents and combine with only one molecule of the chloride ; 6-nitrocoumarin does not react. The compound from coumarin is more stable being unaffected by boiling water

whereas the product from 7-methylcoumarin is far less stable. By the action of aqueous sodium hydroxide and hydrogen sulphide they give the corresponding coumaric acids. In view of these properties, and the work of Adams *et al*,[1] Middleton,[7] Vorlander,[13] and Wright[14] on similar compounds and the present work on the action of mercuric acetate on coumarins they have to be considered as addition products of mercuric chloride on the double bond (IV). Experiments intended to settle the constitution more precisely were not successful.



IV 3-chloromercuri-4-chloromelilotic anhydride.

Experimental.

Action of Mercuric Acetate.—

(i) *On coumarin.*—Preparation of 3 : 6 : 8-triacetoxymercuri-4-methoxymelilotic anhydride.

Mercuric acetate (4 g.) was dissolved in pure methyl alcohol (80 c.c.) containing a little acetic acid and mixed with coumarin (2 g.) in the same solvent (5 c.c.). The mixture which was quite clear in the cold was boiled on a water-bath under reflux. After about four hours it became milky and when allowed to stand overnight deposited about 0·5 g. of a colourless solid which on analysis gave too high a value for mercury and too low a value for carbon. It was probably contaminated with some mercurous acetate (*compare* Henry and Sharp)[5]. After filtering off this product, heating was continued for further 8 hours when another fraction separated out even from the hot solution. It was filtered, washed repeatedly in the cold with a very dilute solution of acetic acid and subsequently with hot methyl alcohol and dried first in air and finally in a vacuum desiccator. It was a crystalline looking powder, though under the microscope it exhibited no definite shape. (Found : Hg, 63·2 ; C, 20·4 ; $C_{16}H_{16}O_9Hg_3$ required Hg, 63·1 ; C, 20·1%.) The yield of the pure product was about 2·5 g. It turns brown at about 250° and decomposes at 270° and is very sparingly soluble in all the ordinary organic solvents. Though it is unaffected by aqueous sodium carbonate, it dissolves readily in ammonia and sodium hydroxide solutions.

When twice and three times the quantity of mercuric acetate solution was employed, the same product was obtained in greater yield, but its

formation was slower owing to the concentration of coumarin being lower and further it was less pure. If, however, the solution was made more concentrated by employing just enough alcohol to keep the reactants in solution at the beginning when hot, the condensation was faster and the yield better.[6] But the product was not found to be pure even though it was repeatedly washed with alcohol and dilute acetic acid.

The reaction was found to take place even when the solution of mercuric acetate and coumarin in alcohol was allowed to stand at the ordinary temperature of the laboratory (30°). After 2 days, the solution became turbid and in about a fortnight a white crystalline powder (0·5 g.) was obtained. It was found to be identical with the product obtained from heating.

The mercury compound was dissolved in a normal solution of sodium hydroxide, cooled to 0° C. with ice and saturated with hydrogen sulphide. The whole was allowed to stand in the cold chamber overnight, the precipitated mercuric sulphide filtered off and the filtrate acidified with a normal solution of sulphuric acid, the temperature being kept at about 0°. Hydrogen sulphide was removed by passing a current of air through the solution. β-methoxymelilotic acid was precipitated as a white crystalline solid. It was filtered, washed with a small quantity of water and finally crystallised from hot water. It appeared as rhombohedral plates, melted at 122–23°, changed to coumaric acid slowly in the presence of dilute acid or alkali, and was found to be identical with the product obtained by Biilmann's method (*loc. cit.*). The pure dry sample is quite stable and remains unchanged over long periods.

The mercury compound was suspended in glacial acetic acid and a solution of bromine in the same solvent slowly added with vigorous shaking. Bromine was rapidly used up and the addition was stopped when the bromine colour persisted. The mixture was then poured into a large volume of water and the precipitated solid which consisted of a mixture of the bromocompound and mercuric bromide was washed repeatedly with aqueous potassium bromide with a view to remove as much of the mercuric bromide as possible. It was then repeatedly crystallised from boiling glacial acetic acid and was obtained as colourless flat needles, melting at 195°. It was found to be identical with 3 : 6 : 8-tribromocoumarin prepared by direct bromination of coumarin according to the method of Simonis and Wenzel, as shown by mixed melting point, crystalline form, sparing solubility in alcohol and formation with alcoholic potash of 4 : 6-dibromocoumarilic acid.[12]

(ii) *On 7-methyl coumarin.*—Preparation of 3 : 6 : 8-triacetoxymercuri-4-methoxy-7-methyl-melilotic anhydride.

The reaction was carried out under the same conditions as with coumarin. It was much slower since it took 12 hours heating to get the first crop (0·5 g.) and a further 40 hours to get 2·5 g. more. It was purified by first washing with cold dilute acetic acid and subsequently with hot methyl alcohol. After drying in a vacuum desiccator it was found to decompose at 265° without melting. (Found : Hg, 61·7 ; $C_{17}H_{18}O_9Hg_3$ required Hg, 62·2%.) This compound resembled the coumarin derivative closely in all its properties. When hydrogen sulphide was passed into a cold solution of the substance in sodium hydroxide as usual, the corresponding β-methoxy-melilotic acid could not be obtained. On filtering off the mercuric sulphide and acidifying the filtrate, pure 4-methylcoumaric acid was obtained melting at 195° (decomp.). By treatment with bromine in glacial acetic acid a tribromocompound was isolated. It was sparingly soluble in alcohol, but dissolved easily in glacial acetic acid and crystallised in long narrow rectangular plates, melting at 207–8°. (Found : Br, 60·8; $C_{10}H_5O_2Br_3$ required Br, 60·4%.) By analogy with the coumarin compound this is given the constitution 3 : 6 : 8-tribromo-7-methylcoumarin. Since a compound of this formula does not seem to have been recorded in the literature, its preparation by other methods is under investigation.

(iii) *On 6-nitrocoumarin.*—Preparation of 3 : 8-diacetoxymercuri-4-methoxy-6-nitromelilotic anhydride.

Nitrocoumarin (2 g.) was dissolved in methyl alcohol (100 c.c.) and mixed with mercuric acetate (7·5 g.) in the same solvent (150 c.c.) containing a little acetic acid. After the removal of a small precipitate after heating for 4 hours, the clear solution gave 2·5 g. of a yellow crystalline product after boiling for 24 hours and some more was obtained on longer heating. It was purified as usual and dried in a vacuum desiccator. It was definitely yellow, remained unaffected below 300°, was very sparingly soluble in organic solvents and dissolved easily in sodium carbonate, ammonia and sodium hydroxide. (Found : Hg, 54·1 ; $C_{14}H_{13}O_9Hg_2$ required Hg, 54·1%.)

6-Nitro-3 : 8-diacetoxymercuri-4-methoxy-melilotic anhydride was dissolved in fairly strong sodium hydroxide (10% solution), allowed to stand for an hour and then hydrogen sulphide passed. After completely precipitating mercury it was filtered and the filtrate acidified. 5-nitrocoumaric acid was thereby obtained in good yield. If, on the other hand, dilute alkali is used and hydrogen sulphide passed immediately after solution, the resulting acid is contaminated with some amount of 6-nitrocoumarin.

By the action of bromine in glacial acetic acid, the mercury compound yielded a bromoderivative which crystallised from acetic acid in colourless prisms melting at 213–15°. It was identified as 6-nitro-3 : 8-dibromocoumarin by comparison with the compound prepared by the method of Dey and Row.[4]

Action of Mercuric Chloride.—

(i) *On coumarin.*—Preparation of 3-chloromercuri-4-chloromelilotic anhydride.

The method of Clayton (1908), using ether as a solvent, is inconvenient owing to the small solubility of mercuric chloride in it. Acetone and methyl alcohol are better. The easiest procedure is to dissolve coumarin and mercuric chloride separately in the minimum of acetone, mix the two solutions and add water to the uniform mixture. The product separates out as a mass of colourless needles, melting at 165° and identical with the compound obtained from ether. It is filtered and washed with water. It is easily recrystallised from boiling water. (Found : Hg, 47·9 ; $C_9H_6O_2Cl_2Hg$ required Hg, 48·0%.) Though the compound is stable in boiling water, it is easily decomposed by boiling 2 per cent. aqueous hydrochloric acid as shown below :

3-Chloromercuri-4-chloromelilotic anhydride (1 g.) is boiled with 2 per cent. hydrochloric acid (20 c.c.) when it quickly goes into solution. The heating is continued for ten minutes longer and the solution allowed to cool. Coumarin, that is first formed as a liquid, gradually turns into a crystalline solid melting at 70°.

When small quantities of the compound are treated with dilute aqueous alkali, coumaric acid could be easily obtained as shown below : About 0·2 g. of the compound is suspended in water, and dilute caustic soda added. There is a rapid precipitation of yellow mercuric oxide. After about 10 minutes, the solution is filtered and acidified. The crystalline solid that separates out is purified by dissolving in sodium carbonate and reprecipitating. It melts at 208–10° and is found to be pure coumaric acid. But when larger quantities are employed the resulting acid is impure melting at about 185°, and is found to contain mercury. In such cases, the alkali solution is treated with hydrogen sulphide, the precipitated mercury sulphide is filtered off and the filtrate acidified, when pure coumaric acid is obtained.

(ii) *On 7-methylcoumarin.*—Preparation of 3-chloromercuri-4-chloro-7-methylmelilotic anhydride.

The addition compound in this case is unstable in the presence of water even in the cold and heating produces considerable decomposition. It

is, therefore, necessary to avoid water in its preparation. Besides ether (Clayton, *loc. cit.*) acetone can be used. Instead of adding water the acetone mixture is simply allowed to concentrate. The product is obtained as sheaves of colourless flat needles, melting at 173–74° and identical with the compound described by Clayton. It decomposes completely in about a minute in boiling 1% hydrochloric acid giving rise to 7-methylcoumarin. 4-methylcoumaric acid can be easily obtained by the action of sodium hydroxide and hydrogen sulphide.

6-nitrocoumarin does not react with mercuric chloride in acetone solution either in the cold or on heating. Ether is not a suitable solvent owing to the insolubility of nitrocoumarin in this solvent.

Summary.

In methyl alcoholic solution coumarin reacts with mercuric acetate to form 3 : 6 : 8-triacetoxymercuri-4-methoxymelilotic anhydride. By the action of sodium hydroxide and hydrogen sulphide β-methoxymelilotic acid is obtained from it and by the action of bromine 3 : 6 : 8-tribromocoumarin. 7-methylcoumarin behaves similarly giving a trimercury compound. 6-nitrocoumarin forms 3 : 8-diacetoxymercuri-6-nitro-4-methoxymelilotic anhydride which, with alkali and hydrogen sulphide, gives 5-nitrocoumaric acid and with bromine 3 : 8-dibromo-6-nitrocoumarin. It is therefore established that mercuric acetate reacts with the double bond in these coumarins and further mercurates the benzene ring in positions 6 and 8 if they should be free. Mercuric chloride adds on to the double bond in coumarin and 7-methylcoumarin. The reactions of these addition products have been studied. 6-nitrocoumarin does not react with this reagent.

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ON SUMS OF POWERS.

By Inder Chowla.

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(Communicated by Dr. S. Chowla.)

We write $\beta(k)$ for the least value of n such that

$$\sum_{s=1}^{m} x_s^k = \sum_{t=1}^{n} y_t^k \tag{1}$$

is possible in positive integers x_s $(s \leqslant m)$, y_t $(t \leqslant n)$ with $m < n$. When $(x_1, \cdots, x_m) = (y_1, \cdots, y_n) = 1$ we shall express the possibility of (1) by the notation

$$(m)^k = (n)^k. \tag{2}$$

In a series of recent papers Rao[1] has shown that

$$\beta(k) \leqslant k - 1 \tag{3}$$

for $4 \leqslant k \leqslant 8$; he has also obtained numerous relations of the type

$$(5)^7 = (5)^7, \quad (2)^9 = (12)^9, \text{ etc.} \tag{4}$$

All these results were obtained by the method of direct calculation. In this paper we use Tarry's process (*see* Wright 1, 2) which involves only the simplest calculations, to obtain some *new* results of the same type, namely,

Theorem 1.

$$(6)^9 = (8)^9$$

i.e., $\beta(9) \leqslant 8$

Thus (3) *is true for* $k = 9$.

Theorem 2.

$$(7)^9 = (7)^9$$

It is likely that $\beta(k) \leqslant k-1$ *for all* k, *but from Vinogradow's method we can only deduce that* $\beta(k) = 0(k \log k)$.

Notation. Let

$$a_1, \cdots, a_n \underset{k}{=} b_1, \cdots, b_n \tag{5}$$

signify that

$$\sum_{r=1}^{n} a_r^m = \sum_{r=1}^{n} b_r^m \qquad (1 \leqslant m \leqslant k) \tag{6}$$

Thus it is obvious that

Lemma 1. (5) *implies that*

$$\sum_{r=1}^{n} (x + a_r)^s = \sum_{r=1}^{n} (x + b_r)^s. \qquad [1 \leqslant s \leqslant k]$$

Lemma 2 (*Tarry*). *If*

$$a_1, \cdots, a_n \underline{\underline{k}} b_1, \cdots, b_n$$

then

$$a_1, \cdots, a_n, b_1 + x, \cdots, b_n + x \underline{\underline{k+1}} b_1, \cdots, b_n, a_1 + x, \cdots, a_n + x.$$

Lemma 3 (*Tarry*).

$$1, 5, 10, 24, 28, 42, 47, 51 \underline{\underline{7}} 2, 3, 12, 21, 31, 40, 49, 50.$$

Lemmas 1 and 2 are immediately obvious on comparing coefficients of powers of x. For lemmas 1 to 3 see also Dickson 1, Wright 1, 2 and I. Chowla 1, 2.

Proofs of Theorems 1 *and* 2.

Applying lemma 2 to lemma 3 with $k = 7$ and $x = 19$, we get

(7) $$1, 5, 10, 22, 28, 42, 51, 59, 68, 69$$
$$\underline{\underline{8}} 2, 3, 12, 20, 29, 43, 49, 61, 66, 70.$$

Applying lemma 2 to (7) with $k = 8$ and $x = 17$, we get

(8) $$1, 5, 10, 19, 28, 37, 42, 46, 51, 60, 69, 78, 83, 87$$
$$\underline{\underline{9}} 2, 3, 12, 18, 27, 39, 43, 45, 49, 61, 70, 76, 85, 86.$$

Applying lemma 2 to (8) with $k = 9$ and $x = 9$, we get

(9) $$1, 5, 11, 21, 36, 42, 48, 52, 54, 58, 79, 83, 94, 95$$
$$\underline{\underline{10}} 2, 3, 14, 18, 39, 43, 45, 49, 55, 61, 76, 86, 92, 96.$$

Applying lemma 1 to (9) with $x = -47$, we get

(10) $$-46^s - 42^s - 26^s + 1^s + 7^s + 32^s + 47^s + 48^s$$
$$= -44^s - 33^s - 4^s + 14^s + 39^s + 49^s. \qquad [s = 1, 3, 5, 7, 9]$$

or

(11) $$1^s + 4^s + 7^s + 32^s + 33^s + 44^s + 47^s + 48^s$$
$$= 14^s + 26^s + 39^s + 42^s + 46^s + 49^s. \qquad [s = 1, 3, 5, 7, 9]$$

The special case $s = 9$ of (11) implies

(12) $$(6)^9 = (8)^9$$

i.e.,

(13) $$\beta(9) \leqslant 8.$$

Applying lemma 1 to (9) with $x = -\frac{97}{2}$, we get

$$(14) \quad 7^s + 11^s + 19^s + 61^s + 69^s + 91^s + 93^s = 1^s + 13^s + 25^s + 55^s + 75^s + 87^s + 95^s. \quad [s = 1, 3, 5, 7, 9]$$

The case $s = 9$ of (14) implies

$$(15) \quad (7)^9 = (7)^9$$

Thus theorems 1 and 2 are completely proved.

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NOTE ON WARING'S PROBLEM.

By S. Chowla.

(From the Government College, Lahore.)

Received July 3, 1936.

1. Let $f(m)$ denote the number of representations of m as a sum of k non-negative kth powers. On the assumption that $f(m) = O(m^{\epsilon})$ for every positive ϵ, Hardy and Littlewood proved that $G(k) \leq 4k$. Mahler has recently made the surprising observation (based on a simple algebraic identity) that this assumption is false for $k = 3$. It is therefore of interest to know whether the results of Hardy and Littlewood based on "Hypothesis K" can be proved under a less drastic assumption. Dr. Walfisz remarked to me in a recent letter that we can obtain these results on the less stringent hypothesis that

$$\sum_1^x f^2(m) = O(x^{1+\epsilon}) \tag{1}$$

for every positive ϵ. It is the sole purpose of this note to embody a slight generalisation of this remark in the form of the

Theorem. If there exists a number $n = n(k)$ *such that*

$$\sum_1^x f^2(m)\,(x - m)^n = O(x^{n+1+\epsilon}) \tag{2}$$

for every positive ϵ, then

$$G(k) \leq \text{Max}\,[2k + 1, \Gamma(k)] \tag{3}$$

Proof.—A reference to P. N. VI shows that

(3) is true if

$$\sum_1^\infty f^2(m)x^{2m} = O\{(1 - x)^{-1-\epsilon}\} \tag{4}$$

for every $\epsilon > 0$ $(0 < x < 1)$. But (4) is certainly true if (2) is true. Hence our result.

POLARISATION OF RAMAN LINES IN SOME INORGANIC ACIDS.

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1. Introduction.

A considerable volume of experimental data has been obtained in recent years from the study of the Raman spectra regarding the progressive dissociation of strong electrolytes in concentrated aqueous solutions. It has been found that changes from the covalent to the electrovalent form take place in them in a manner not contemplated by the Debye-Hückel theory of complete ionisation, the point of transition depending on the strength of the acid and the state in which it exists. Thus the halogen hydrides give rise to Raman lines when they are in the state of solid, liquid or vapour or in solution in non-polar solvents[1] indicating that they are covalent in such cases; but even in concentrated solutions in water or other polar solvents they change to the electrovalent form and consequently do not yield any line. On the other hand, the monobasic acids like nitric[2] or iodic[3] acids yield a large number of Raman lines the relative intensities of which change according to the degree of concentration of the acid in water and are interpreted on the assumption that in the more concentrated solutions the percentage of undissociated molecules is great and goes on diminishing with dilution. The polybasic acids, namely, sulphuric,[4] selenic,[5] selenious[6] and phosphoric acids,[7] likewise reveal that the dissociation is not only progressive but stepwise in character and is a function of concentration.

Though the changes in the relative shifts and intensities of the Raman lines at various dilutions of these acids have been qualitatively interpreted as due to progressive ionisation, no attempt has hitherto been made to assign

1 West, Wm., and Arthur, P., *Jour. Chem. Phys.*, 1932, **2**, 215.
2 Rao, I. R., *Proc. Roy. Soc.*, A, 1930, **127**, 279.
3 Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 119.
4 Nisi, H., *J. J. Phys.*, 1929, **5**, 119.
5 Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 307.
6 Venkateswaran, C. S., *Ibid.*, 1936, **3**, 533.
7 Venkateswaran, C. S., *Ibid.*, 1936, **3**, 25.

the lines to any particular mode of oscillation of the molecular species concerned. For this purpose it appears necessary to have a knowledge of the state of polarisation of the lines themselves. A proper identification of frequencies corresponding to similar modes of oscillation in the different units arising from the ionisation of the molecules could also be expected to give us a better knowledge of the mechanism of the changes that take place in the molecule undergoing dissociation. The present paper concerns itself with the state of polarisation of the Raman lines of nitric, iodic, sulphuric, selenic and selenious acids and its significance in relation to the molecular structure of these acids.

2. *Experimental Arrangements and Results.*

The acids used in the investigation were all taken from freshly opened bottles of the purest stock of Kahlbaum chemicals and were fairly free from dust. The iodic and the selenious acids were crystallised out of carefully filtered aqueous solutions and redissolved in double-distilled water. A few drops of nitric acid were added to concentrated sulphuric acid in order to render the latter free from fluorescence.[8] A Hewittic quartz mercury burner served as the source of illumination and was focussed by means of a large glass condenser on the Raman tube which was held horizontally along the axis of the spectrograph. The horizontal and the vertical components of the scattered radiation were separated by interposing a suitably oriented large quartz double-image prism between the slit of the spectrograph and the observation end of the tube. The two components were focussed one above the other on the slit and recorded simultaneously and for the same time on the photographic plate. Specially backed Ilford golden isozenith plates were used and the developing solution and the time of development were kept identical throughout. The ratio of intensities of the horizontal and the vertical components of each of the Raman lines was determined with the help of a Moll microphotometer. Since a high degree of accuracy in the depolarisation measurements is not attempted the intensities of lines excited by 4358 radiations of the source in the various plates were read off from the same density log intensity curve of the microphotometer for the 4600 region of the spectrum. In view of the fact that only the ratio of the intensities of the two components appearing at constant wave-length is desired, the error introduced by the variable sensitiveness of the photographic plate is not considerable. As has been pointed out by previous investigators,[9] the state of polarisation determined in this manner would involve errors due to

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[8] Médard, L., *Compt. Rend.*, 1934, **199**, 1615.

[9] Bhagavantam, S., *Ind. Jour. Phys.*, 1930, **5**, 59.

lack of strict transversality between the directions of incidence and observation and also due to oblique refraction at the surface of the prisms. These errors were determined as follows :—The polarisation characters of the principal Raman lines of CCl_4 were ascertained under identical circumstances and assuming the known values of polarisation of these lines the required error was evaluated. The results given in the present paper give the upper limit of the depolarisation ratios of the lines and are probably correct to $\pm 5\%$.

The results are given in Tables I—V. The frequency ν in cm.$^{-1}$ of the line is given in the first column, the intensity I of the line in the second and the corrected depolarisation ratio ρ in the third. In the case of extremely weak lines, the state of depolarisation is indicated by D and P where D

TABLE I (*a*).

Nitric Acid 70%.

No.	1	2	3	4	5
ν in cm.$^{-1}$ ..	638	697	924	1050	1126
I	4	6	6 br	10	1
ρ	0·71	0·62	0·17	0·17	0·70
ρ (Previous) ..	0·30	0·20	0·20	0·10	..

No.	6	7	8	9	10
ν in cm.$^{-1}$ ..	1297	1389	1537	1611	1699(?) 3466
I	8 br	2 br	1	2	3
ρ	0·30	0·63	$\lesssim$0·8	0·5	0·3
ρ (Previous)	0·10	..	..	..	..

TABLE I (*b*).

Nitric Acid 25%.

No.	1	2	3	4	5	6
ν in cm.$^{-1}$ ..	726	924	1048	1297	1389	Water band
I	3	0	10	2	3 br	Strong
ρ	$\lesssim$0·82	P	0·16	P	$\lesssim$0·85	0·55

TABLE II.

Iodic Acid 6 N.

No.	1	2	3	4	5	6
ν in cm.$^{-1}$ ..	330	463	644	789	823	Water band
I	8	1	6	10	6	Medium strong
ρ	0·60	P	0·30	0·25	0·25	0·60

TABLE III (*a*).

Sulphuric Acid 99%.

No.	1	2	3	4	5	6	7	8
ν in cm.$^{-1}$ ..	384 to 434	564	916	970	1045	1140	1364	1398 (N_2O_5)
I	4 br	6	10	0	4	4 br	0	2
ρ	0·7—0·75	≶0·81	0·16	D	0·32	0·62	D	0·20

TABLE III (*b*).

Sulphuric Acid 25%.

No.	1	2	3	4	5
ν in cm.$^{-1}$ ..	427	593	896	982	1047
I	3	4	2	6	6
ρ	>0·75	>0·76	0·17	0·03	0·24
No.	6	7	8	9	
ν in cm.$^{-1}$ ..	1172	1223	1334	Water band	
I	1	1	2	Strong	
ρ	D	D	0·77	0·56	

TABLE IV.

Selenic Acid (molten).

No.	1	2	3	4	5	6	7
ν in cm.$^{-1}$ ..	294	361	388	756	914	996	1105 } 1186 }
I	3	6	6	10	8	3	0
ρ	D	>0·76	>0·77	0·30	0·30	0·70	0·5

TABLE V.

Selenious Acid (molten).

No.	1	2	3	4	5	6	7
ν in cm.$^{-1}$ ..	238	343	380	545	690	862	910
I	1	4	3	1	10	10	3
ρ	D	>0·79	$\lesssim$0·81	P	0·5	0·5	0·44

means that the depolarisation ratio is nearly equal to 6/7 and P means that it is less than 6/7.

3. Discussion of Results.

Nitric Acid.—The Raman spectrum of this acid has been investigated thoroughly from the point of view of electrolytic dissociation by numerous investigators notably by Rao[10] and recently by Médard.[11] Dadieu and Kohlrausch[12] have examined the acid with special reference to its constitutional form. In general, the concentrated solution of this acid yields ten Raman lines with the following mean frequency shifts :—638 (4), 697 (6), 924 (6 br.), 1050 (10), 1126 (1), 1297 (8 br.), 1389 (2 br.), 1537 (1), 1611 (2) and 1699 (4). At a concentration of about 25% all except three lines at 726, 1048 and 1389 practically disappear and hence are attributed to the undissociated molecule. The latter three lines which are also present in the solutions of nitrates are assigned to the nitrate ion. Very intense photographs of the Raman spectra of this acid obtained by the author and reproduced in the accompanying plate confirm the above results of the previous investigators.

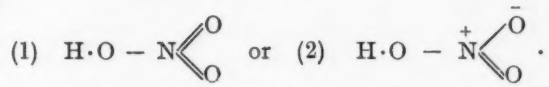
[10] Rao, I. R., *Loc. cit.*

[11] Médard, L., *Compt. Rend.*, 1934, **198**, 1407.

[12] Dadieu and Kohlrausch, *Naturwissenschaften*, 1931, **19**, 690.

The state of polarisation of these lines of the acid at the two specified concentrations is given in Table I. The results of a previous investigation of the polarisation of some of the lines of the 70% acid by Venkateswaran[13] are given in the fourth column and reveal large differences which cannot be explained mainly by the errors of measurement. As is to be expected from the plane symmetrical structure of the NO_3' ion the single and parallel vibration with a frequency shift of 1048 cm.$^{-1}$ is more or less completely polarised and the two doubly degenerate and perpendicular vibrations at 726 and 1389 are completely depolarised.

From the fact that the lines 726 and 697 possess different degrees of depolarisation they are to be considered as belonging to entirely independent vibrations and not as one line undergoing a change in frequency due to dilution. Thus there are eight remaining lines belonging to the undissociated nitric acid molecule. It has been pointed out by Dadieu and Kohlrausch that in agreement with Hantzsch's theory of pseudo-acids, the Raman spectrum of nitric acid gives evidence for the existence of the molecules in it having a form $HO.NO_2$. The structural formula should in that case be written as



In both forms the nitrogen atom can occupy a position either in the plane of the oxygen atoms as in the nitrate ion or at the apex of a pyramid. Thus if we assume that the strength of normal covalent bond between two atoms is different from that of a co-ordination bond between the same two atoms and neglect for a moment, the influence of the hydrogen atom, the first form of the molecule could be treated as AB_2B' type and the second form as AB B'B" type. E. B. Wilson[14] has calculated the number and the state of polarisation of the normal vibrations of these types on the basis of the selection rules for the Raman and the infra-red discussed by Placzek and has shown that there will appear six lines in both these types; but for the AB_2B' type the depolarisation ratio will reach the limiting value of 6/7 for three of these lines if A is in the plane of the B atoms and for two lines if A is at the apex of a pyramid. For the ABB'B" type where all the B atoms are dissimilar, only one of the lines will be completely depolarised if the molecule is plane and none at all if the molecule is pyramidal. In the nitric acid molecule besides these six normal vibrations, there should also be two lines belonging to the co-valent OH group, one of which is the valence oscillation

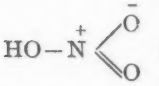
[13] Venkateswaran, S., *Phil. Mag.*, 1933, **15**, 263.

[14] Wilson, E. B. (Jr.), *Jour. Chem. Phys.*, 1934, **2**, 432.

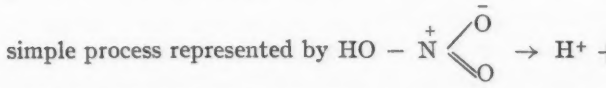
which will be highly polarised and the other, the deformation oscillation which will be unpolarised. As indicated before in the concentrated solution of the acid these eight lines have been observed besides those due to the NO_3' ion, of which only one line at 1538 possesses a depolarisation ratio of 6/7. The line 1699 which has been reported for the $HO.NO_2$ molecule, possesses a low depolarisation ratio of less than 0·3 and is most probably wrongly assigned by Angus and Leckie to the 4358 radiations of the source.[15] The high degree of polarisation suggests that it is the valence oscillation of the hydroxyl group and its frequency shift is not 1699 but is 3466 $cm.^{-1}$ with 4046 as the exciting line, and is of the order of the OH frequency in the hydroxides and alcohols. The line 1538 which is weak and highly depolarised is also to be attributed to the deformation oscillation of the OH group.

All the other six remaining frequencies, namely, 638, 697, 924, 1126, 1297 and 1611, are polarised to some extent or other and therefore belong to a configuration AB_3 where all the B atoms are different and A is at the apex of a pyramid. Two of these frequencies, namely, $\omega_1 = 1297$ and $\omega_2 = 924$ which are the strongest of the group, are depolarised to an extent of only 0·30 and 0·17 respectively and are therefore due to the two parallel vibrations of the AB_3 type. The rest four are due to the four perpendicular vibrations.

Thus it is to be concluded that the nitric acid molecule has a structure



and that in the process of dissociation a great change takes place in the NO_3 group from a pyramidal to a plane equilateral type. If the plane structure were preserved in the undissociated molecule also, we could expect only a small change in the frequency shift of the parallel vibration of the NO_3 ion due to the ionisation of the hydroxyl group. The fact that the shift from $\omega_1 = 1297$ in the acid molecule to $\omega_1 = 1050$ in the ion is great, lends further support to the above conclusion. During the ionisation a simple process represented by



would make the nitrate ion unsymmetrical which is not supported by X-ray and Raman measurements. It is probable that the ionisation is accompanied by a rearrangement of electronic configuration of the nitrate group rendering the three oxygen atoms identical. Such a process may be

[15] Angus, W. R., and Leckie, A. H., *Proc. Roy. Soc.*, A, 1935, **149**, 327.

visualised by postulating that NO_3' ion is represented by $\overset{-}{O} - \overset{++}{N}\begin{matrix}\overset{-}{O} \\ \overset{-}{O}\end{matrix}$ or that the double bond of one of the oxygen atoms is labile.

Iodic Acid.—For a 6 N solution of iodic acid the author has reported in a previous paper[16] five broad lines, namely, 330, 463, 644, 789 and 823. The band 789 is shown to be composed of two frequencies 789 and 796 and the band 330 of two lines at 328 and 377. Of these lines 789, 644, 463 and 330 are assigned to HIO_3 molecule, the line 823 to the polymerised ion I_2O_6'' and the line 796 to the IO_3' ion. The results given in Table II show that all these lines are polarised to varying degrees. The two lines possessing maximum polarisation are to be attributed to the two parallel vibrations of a pyramidal molecule of the form $HO - \overset{++}{I}\begin{matrix}\overset{-}{O} \\ \overset{-}{O}\end{matrix}$. The other lines 463 and 330 whose degree of depolarisation is higher probably belong to the perpendicular vibrations. Vibrations similar to the latter in nitric acid have a higher depolarisation ratio. It is probable that in the case of iodic acid, the depolarisation ratio of the 330 band is lowered by the presence of a parallel vibration belonging to the IO_3' ion in that region. The line at 823 which has been assigned to the polymerised radical I_2O_6'' also shows a high percentage of polarisation and therefore belongs to the symmetrical oscillations of that group.

It is interesting to observe that the frequency shift 789 corresponding to the parallel vibration in the iodic acid molecule suffers only very little change in passing to the iodate ion. This is partly due to the fact that in both states the molecular form remains pyramidal and partly due to the increased mass of the central atom.

Sulphuric Acid.—The early investigations of the Raman spectrum of this acid were of an unsatisfactory nature due to the presence of a strong fluorescence in the scattered radiations which masks all but the intense lines in the concentrated solutions. By oxidising the traces of organic impurities by a few drops of $KMnO_4$ or HNO_3 Médard[17] has been able to get rid of this fluorescence and to obtain a clear spectrum for the acid. By a similar method the author has obtained a fairly intense picture for 99% and 25% acid and the frequency shifts of the lines observed agree fairly well

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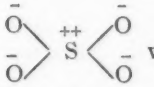
[16] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 119.

[17] Médard, L., *Compt. Rend.*, 1933, **197**, 582; 1934, **198**, 1407.

with those of Médard. In general, the 99% acid gives seven lines at 384-434 (4 br.), 564 (0), 916 (10), 970 (0), 1045 (4), 1140 (4 br.) and 1364 (0). Besides, a sharp line attributed to N_2O_5 also appears at 1398. Of these 384–434 shows a doublet structure which is confirmed further, by the different states of polarisation of the component parts. New lines that arise on diluting the acid with water are given in Table III(*b*).

According to classical literature, sulphuric acid is represented by the structural formula , where sulphur has sexavalency as in SF_6. The SO_4'' ion, formed after complete ionisation, possesses a symmetrical structure represented according to modern electronic conceptions as,  where all the four oxygen atoms are identical in agreement with the perfectly tetrahedral structure attributed to it. The mechanism of transition from the undissociated molecule to the dissociated SO_4'' ion is by no means clear.

The four frequencies which are present in the solutions of sulphates and attributed to the sulphate ion are 418, 597, 982 and 1168. Among the lines obtained for 25% acid, the intense line at 982 is more or less completely polarised and represents the symmetrical expansion and contraction of the perfectly tetrahedral SO_4'' ion. As is to be expected the other three degenerate frequencies 427, 593 and 1172, all belonging to the SO_4'' ion are depolarised more or less to an extent of 6/7.

The frequencies 384–434 and 564 appear to be common to the undissociated H_2SO_4 molecule and to the HSO_4' ion as well as to the SO_4'' ions.[18] Of the remaining frequencies cited in Table III, those at 916, 970, 1140 and 1364 belong to the undissociated molecule. If we assume that the latter is a distorted tetrahedron like CH_2Cl_2 with two oxygen atoms placed above sulphur and the two hydroxyl groups below, we can expect nine frequencies[19] in Raman effect of which five will be depolarised. The intense line at 916 shows a high degree of polarisation and evidently corresponds to the breathing frequency* of such a structure. As mentioned before, 384–434 is a doublet

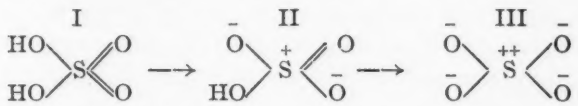
[18] Woodward and Horner, *Proc. Roy. Soc.*, A, 1934, **144**, 129.

[19] Wilson, E. B., *Loc. cit.*

* The term 'breathing frequency' in these pages refers to the vibration in which the tetrahedron contracts or expands as a whole.

and the ratio of depolarisation of the components is distinctly lower than 6/7. The broad line 1140 is also polarised. These four, thus, represent the polarised vibrations of the distorted tetrahedron. Three out of the five depolarised vibrations are 564, 970 and 1364 and the remaining two are probably too feeble to be recorded on the plate.

The lines which are known to belong definitely to HSO_4' ions are 1045, 1223 and 1334. Of these the most intense line at 1045 possesses a depolarisation ratio of about 0·24 and evidently corresponds to the expansion and contraction of the tetrahedron. It is interesting to observe that the depolarisation ratio of the breathing frequency which is almost zero in the SO_4'' ions is about 0·17 in the undissociated molecule and attains a value of more than 0·24 in the HSO_4' ions. If we assume that the extent of polarisation is a measure of the symmetry of structure of the molecular species, we are led to infer that HSO_4' ion is the most asymmetrical of the three. A mechanism which could satisfactorily explain these experimental results may be outlined as follows :—

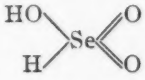
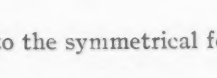
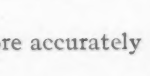


The undissociated molecule having a structure given by formula I changes to form II after the first stage of ionisation and on further dissociation yields the symmetrical SO_4'' ion. The tetrahedral structure is preserved throughout ; but as may be easily seen the middle form representing HSO_4' ion has the least symmetry.

Selenic Acid.—In a detailed investigation of the Raman spectrum of selenic acid,[20] it has been pointed out that it behaves in Raman effect in a manner analogous to sulphuric acid and it is gratifying to note that the polarisation characters of the lines also correspond closely to that of the latter. The molten acid yields eight lines of frequency shifts 294 (3), 361 (6), 388 (6), 756 (10), 914 (8), 996 (3), 1105 (0) and 1186 (0). Of these 756, 996 388, 361 and 294 as well as 1105 and 1186 have been assigned to H_2SeO_4 molecule and 914 to the $HSeO_4'$ ion. If we assume the tetrahedral structure to H_2SeO_4 molecule and its dissociation products, the high degree of polarisation of 756 and 914 shows that they represent the symmetrical vibrations of H_2SeO_4 molecule and $HSeO_4'$ ion respectively. The polarisation characters of the other lines follow, in general, closely those of the corresponding

[20] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 307.

lines of sulphuric acid. But the greater asymmetry of the $HSeO_4'$ ion is not so clear as in the case of HSO_4' ion.

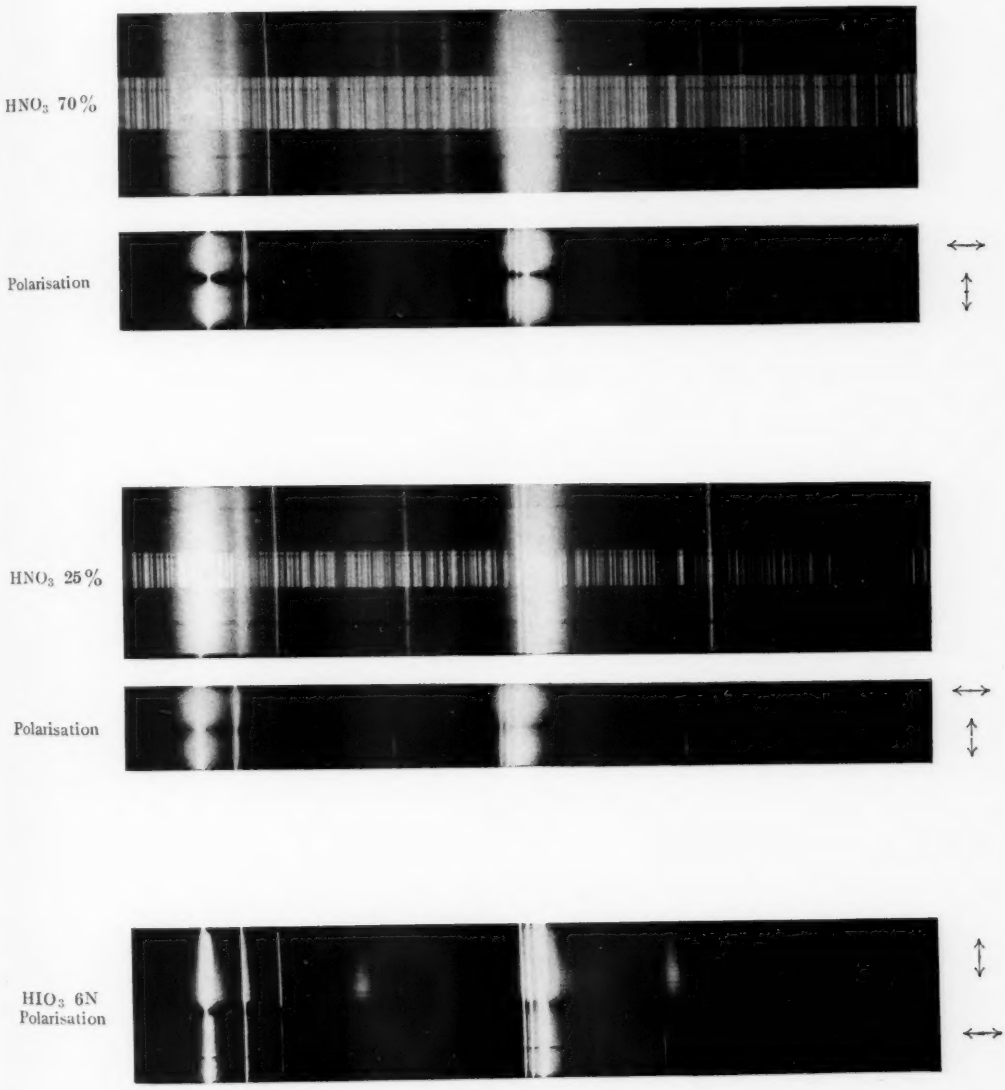
Selenious Acid.—The six frequencies reported previously[21] for the molten liquid are 238 (1), 343 (4), 380 (3), 545 (1), 690 (10) and 892 (10). The polarisation picture shows that the band 892 consists of two components with frequency shifts of 862 and 910 and are, therefore, listed separately in Table V. The broad lines 343 and 380 show a depolarisation of 6/7 and hence confirm their assignment to the lower degenerate vibrations of the molecular species which are assumed to possess a pyramidal structure. The line 545 is attributed to the unsymmetrical form  and the line 690 to the symmetrical form  . Both these lines are polarised indicating that they correspond to the vibrations having maximum symmetry in the respective molecules ; but their relative degree of depolarisation could not be determined due to the extreme feebleness of the line 545 in the molten liquid. The high degree of polarisation of 862 shows that $HSeO_3'$ ion is more symmetrical than the undissociated molecule and is, therefore, probably more accurately represented by the formula  .

In conclusion the author wishes to express his heartfelt thanks to his professor Sir C. V. Raman for his constant interest in the work.

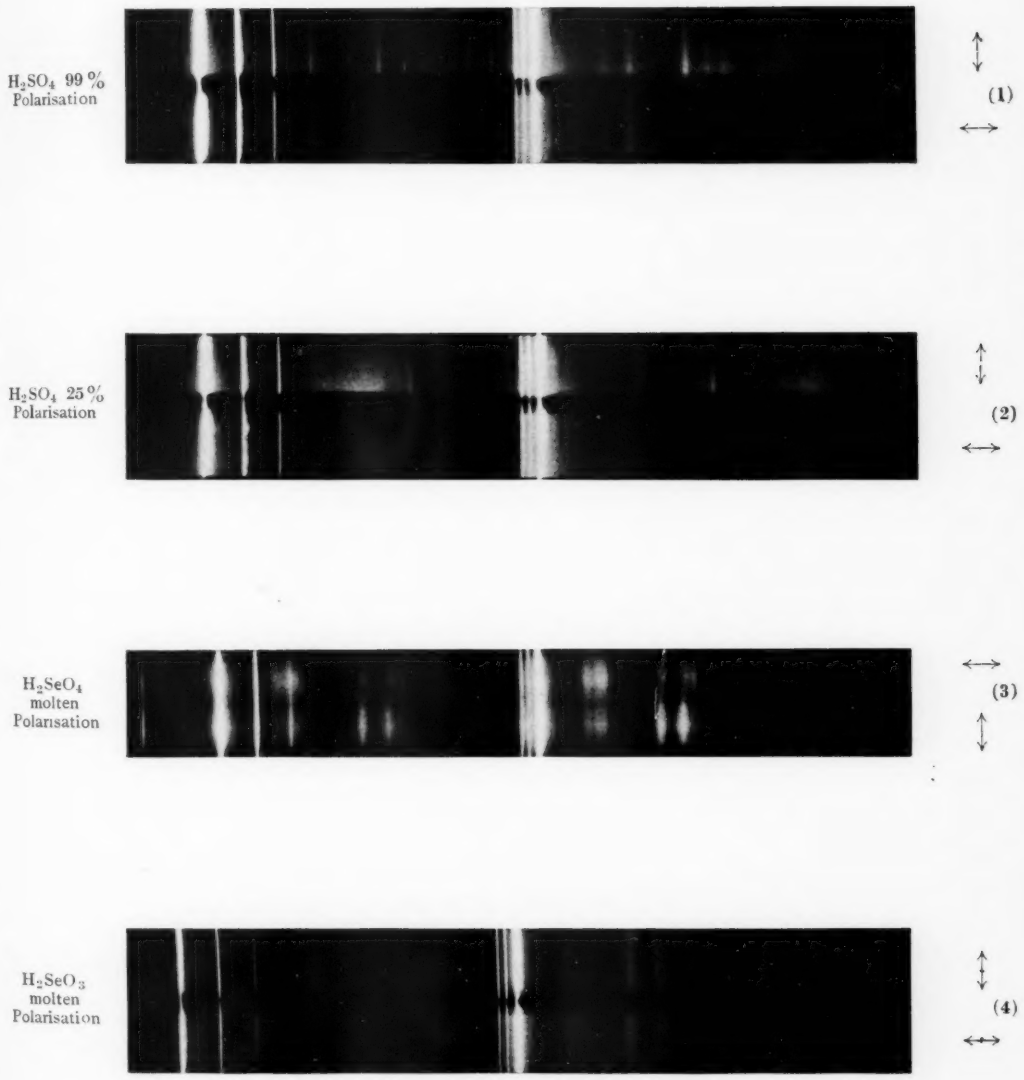
Summary.

The polarisation of Raman lines of nitric, iodic, sulphuric, selenic and selenious acids is investigated making use of the usual double-image prism method. All the lines of the concentrated nitric acid except one at 1538 which is attributed to the deformation oscillation of the hydroxyl group, show varying degrees of depolarisation which are less than the limiting value 6/7. The lines due to the nitrate ion possess a state of polarisation which is in agreement with the plane equilateral structure attributed to it. From the results of polarisation six lines belonging to the undissociated nitric acid molecule are identified with the known modes of oscillation of an unsymmetrical pyramidal model having a structure . The

[21] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 533.



Raman Spectra—Polarisation



Raman Spectra—Polarisation

state of polarisation of the Raman lines of the H_2SO_4 molecule and its dissociation products, HSO_4' and SO_4'' ions generally supports the assumption that all the three forms are tetrahedral and that HSO_4' ion is the most distorted of the three. Structural formulæ of the three species and the mechanism of dissociation from one form to the other are discussed in relation to the degree of depolarisation of the breathing frequency. Polarisation of the Raman lines of selenic acid is analogous to those of sulphuric acid. The results of polarisation of the bands of iodic acid as well as selenious acid generally support the previous assignments of these bands to different molecular species.

MAGNETISM AND COLD-WORKING IN METALS.

Part II. Single Crystals of Bismuth, Zinc and Tin.

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Received June 29, 1936.

1. Introduction.

In Part I[1] of this series, the results of the magnetic investigations of cold-worked polycrystalline rods of bismuth, zinc, cadmium and tin were given. The diamagnetic susceptibility of bismuth was found to be lowered effectively by the application of tensional stress. Zinc and cadmium, on the other hand, showed a small decrease. The paramagnetic susceptibility of white tin gradually decreased as the density of the metal was lowered and even changed sign below a specific density value. These results were considered in the light of the theories relating to polycrystalline structure in metals. It was shown that the application of stress resulted in the formation of more amorphous matter on the planes of slip between the innumerable small crystals and also in the production of deformation in these crystals. Each of these effects was shown to have an influence on the susceptibility of the metals.

The investigations also showed that the observed changes of susceptibility were almost proportional to the changes of density accompanying cold-working. Attention was also drawn to the theories of Honda and Shimizu[2] attributing the susceptibility changes to the decrease in the number of free electrons and increase in the number of bound electrons when the metal is cold-worked. While the theory is no doubt applicable in the case of allotropic transformation or melting,[3] doubts may be raised regarding the direct applicability of the theory to the case of cold-worked polycrystalline metals in view of their discontinuous structure.

These considerations naturally lead one to an investigation of the effects arising from cold-working on single crystals of metals. In this paper, single crystals of bismuth, zinc and tin have been investigated.

2. Experiment.

(*a*) *Preparation of single crystals.*—Single crystals of these metals were prepared by the method of Bridgman[4] of slow cooling, used also by McLennan, Ruedy and Cohen[5] for zinc and cadmium, Goetz and Focke[6] for bismuth and Rao and Subramaniam[7] for thallium. The tube used for the preparation of

the mould was similar to those used in Part I (see Fig. 1). The end A of the tube was drawn sharply to almost a fine point. After cleaning the tube

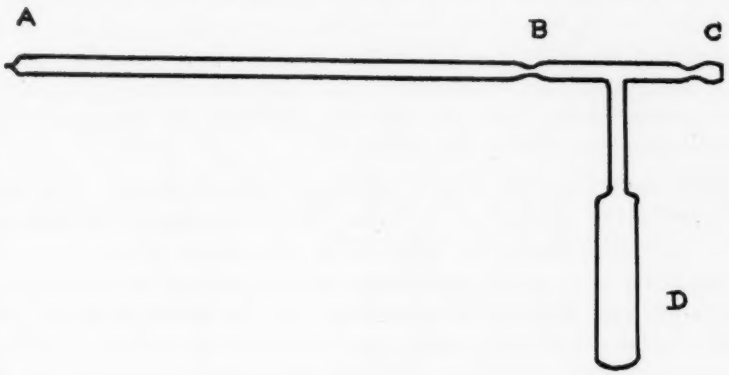

FIG 1.

thoroughly, a sufficient quantity of the metal was taken in D. C was next connected to a Cenco hyvac pump and after lowering the pressure to the lowest possible value, the metal in D was melted with a Bunsen burner. All occluded gases were removed by shaking the molten metal, which was next allowed to run into the tube AB, the entire lengths AB and BD being kept heated by the burner. After cooling, the tube AB was sealed off at the constriction near B.

The tube was next suspended vertically along the axis of an electrically heated furnace, the temperature inside which was regulated to be about 40° above the melting point of the metal investigated. The lowering device consisted of an ordinary time-piece, the setting screw of which was replaced by a cylinder. The length of the circumference of this cylinder gave the rate of lowering which for the metals used here varied from 1·5 to 3 cm. per hour.

After the cooling experiment, the crystals were removed from the glass by cracking all round and breaking away the glass pieces as gently as possible. An examination of the metal cylinder in a beam of light showed at a glance whether it was a single crystal or not.

The crystals were prepared to have lengths varying from 10 to 15 cm. Bismuth and tin crystals had diameters ranging from 4 to 5 mm. while those of zinc had 2 or 4 mm.

(*b*) *Crystal structure.*—As will be explained subsequently, the magnetic measurements showed whether the crystal was single or not. Zinc crystallises

in the hexagonal close-packed system, the a and c values (in Ångstrom units) being 2·649 and 4·930 ($c/a = 1·861$).[8] The basal plane in this crystal is the 0001 plane which is also the cleavage plane when the crystal is broken. The determination of the principal susceptibilities of the crystals requires a knowledge of the angle ϕ made by the hexagonal axis with the cylindrical axis of the crystal. By breaking the crystal after the magnetic investigation, the angle between the basal plane and the cylindrical axis was measured with a spectrometer and thus ϕ was calculated.

Bismuth crystallises with a rhombohedral structure.[9] The cleavage plane is also the basal plane and thus after the magnetic measurements, the crystal could be broken and the angle ϕ estimated as before.

White tin has a body-centred tetragonal structure, the a and c values being 5·818 and 3·174 Å,[10] respectively. If the outer form of a single crystal is represented on the tetragonal axis a, a, c, $\alpha = \beta = \gamma = 90°$, then the most important etch plane formed is the s-plane (101) and the angle between this plane and the (100) plane can be shown[11] to be 68° 54′. This is also the inclination of the tetragonal c-axis with the (101) etch plane. The etching was effected with hydrochloric acid of the proper concentration to give slow etching. The orientation of the etch planes was determined by an adaptation of the Bridgman method.[12] It was thus possible to determine the angle between the tetragonal axis and the cylindrical axis of the crystal.

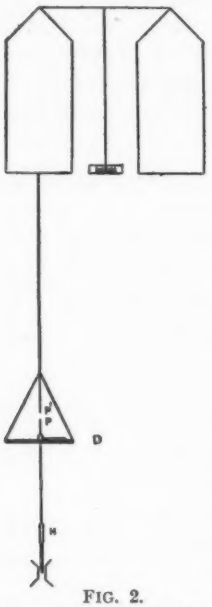

FIG. 2.

(*c*) *Determination of the principal susceptibilities.*—The magnetic investigations were conducted as in Part I by the Guoy method. The specimen was suspended from the right arm of a sensitive analytical balance so that the lower end was symmetrically situated between the pole faces (see Fig. 2). Directly suspended from the pan by a thick wire was a circular disc D graduated on the circumference in degrees. A crystal holder H passed through a snug hole in the disc D and a cross pointer gave the readings on the disc. The top of the holder was sharpened to a point P which was adjusted to be opposite another point P′ attached to the disc support. The adjustments were so made that when the crystal was slipped into the spring holder H and the points P and P′ were opposite to each other, the axis of the crystal cylinder was vertical and the lower face of the crystal symmetrically between the pole faces.

The Guoy forces may be measured for any one crystal at different positions of the pointer on the circular scale D. Measurements were usually taken at intervals of 15° during one complete rotation of the crystal, the current through the elctromagnet being kept steady at 6 amperes. The brass carrier H was of thin sheet metal and the force on it due to the field was carefully measured for the requisite current and due corrections were applied after the Guoy forces on the suspended crystals were determined. This correction was of the order of half a milligram.

The force on a cylindrical specimen of sufficient length and uniform cross-section A is given by

$$F = \tfrac{1}{2} (\kappa - \kappa_a) A (H^2 - H_0^2)$$

where κ and κ_a are the volume susceptibilities of the specimen and the surrounding air respectively. H is the intensity of the magnetic field between the pole faces while H_0 is the intensity of the magnetic field at the upper face of the crystal. Actually, however, H_0^2 is negligibly small when compared with H^2. The value of κ_a at atmospheric pressure and temperature (30° C.) is taken to be $0 \cdot 029^{13}$ from the tables.[14] The force F is determined by weighing the crystal initially and then finding out the change in the balancing weight when the magnetic field is applied.

The important factors which influence the accuracy of the measurements are the values of the field strength H and the mean area of cross-section of the crystals. In these experiments, the cross-sectional area was determined in two ways. First, the mean area of section of the glass tube in which the molten metal was to be solidified was determined with a length of mercury column. Secondly, the volume of the crystal was determined by weighing it in air and in pure benzene (specific gravity = 0·878 at 30° C.), and knowing the length of the cylindrical specimen, the mean area of section was found. The two measurements agreed perfectly. The intensities of the magnetic field at different magnet currents were determined with a search coil and a ballistic galvanometer, the readings of which were standardised with a Hibbert's magnetic standard. The value of H_0 was found for a rod of length 10 cm. to be 1/40 of H and hence H_0^2/H^2 becomes 1/16 per cent. Since all the crystals studied here had lengths greater than 10 cm. H_0^2 was neglected in the calculations.

Test experiments were also conducted using a tube of pure water as outlined in Part I and the results obtained agreed with these measurements within the limits of error.

(*d*) *Theory of the measurements.*—Consider the case of hexagonal crystals.[15] Let SS represent a circular cross-section of the cylindrical crystal and let OP be a section coincident with the basal plane of the crystal

(Fig. 3). OZ and OC are the normals to these sections at O. The angle between these normals is ϕ. The X-axis on the section SS is chosen to lie on the plane ZOC and the angle between OX and the direction of the magnetic field is θ. If the crystal is rotated, the angle θ changes and the susceptibility of the crystal χ_θ in the direction of H varies correspondingly. OC gives the direction of the c-axis of the crystal while OP gives the direction of the a-axis on the hexagonal plane. A reference to the figure shows that OY and the b-axis coincide.

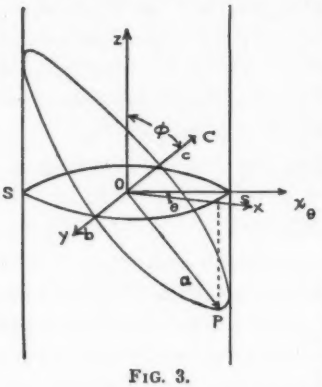

FIG. 3.

If χ_a, χ_b, χ_c are the principal susceptibilities of the crystal, the susceptibility χ_θ in the direction of H making direction cosines α, β, γ with the directions of the principal susceptibilities of the crystal is given by

$$\chi_\theta = \chi_a \alpha^2 + \chi_b \beta^2 + \chi_c \gamma^2 \quad .. \quad .. \quad .. \quad .. \quad (1)$$

Since the crystal has a hexagonal structure, $\chi_a = \chi_b$. Further, since OY and the b-axis coincide, we obtain for χ_θ the following expression if we substitute the values of the direction cosines in terms of θ and ϕ

$$\begin{aligned}\chi_\theta &= \chi_a \cos^2\phi \cos^2\theta + \chi_a \sin^2\theta + \chi_c \sin^2\phi \cos^2\theta \\ &= \chi_a (\cos^2\phi \cos^2\theta + \sin^2\theta) + \chi_c \sin^2\phi \cos^2\theta \quad .. \quad (2)\end{aligned}$$

If χ_0 and χ_{90} be the values when $\theta = 0°$ and $\theta = 90°$ respectively we have

$$\chi_0 = \chi_a \cos^2\phi + \chi_c \sin^2\phi \text{ and } \chi_{90} = \chi_a \quad .. \quad .. \quad (3)$$

If we now designate χ_a and χ_c as $\chi_\perp$ and $\chi_\parallel$ being the susceptibilities perpendicular and parallel to the hexagonal axis,

$$\chi_\perp = \chi_{90} \text{ and } \chi_\parallel = \frac{\chi_0 - \chi_{90}\cos^2\phi}{\sin^2\phi} \quad .. \quad .. \quad .. \quad (4)$$

From these we obtain for χ_θ

$$\chi_\theta = \chi_0 + (\chi_{90} - \chi_0)\sin^2\theta \quad .. \quad .. \quad .. \quad (5)$$

which expresses the variation of χ_θ with θ.

These relations are equally applicable in the case of rhombohedral bismuth and tetragonal tin. The angle is the angle between the normal to the basal plane and the cylindrical axis in the case of bismuth. In the case of tin this becomes the angle between the tetragonal axis and the cylindrical axis.

3. *Results.*

(*a*) *Bismuth.*—We shall first record the results obtained with bismuth. Some of the polycrystalline bismuth rods used in Part I were used for preparing

single crystals. A spectroscopic analysis of the metal was made by taking an arc spectrum and the impurities were found to be copper (less than 0·001%), silver (less than 0·01%) and lead (slightly greater than 0·001%). The results obtained with one of the crystals for which ϕ was 38° 0′ is given below. In the following table are set forth the values of χ_θ for various angles of θ ranging from 0 to 360°.

TABLE I.

θ	χ_θ	θ	χ_θ	θ	χ_θ
0°	— 1·372	120°	— 1·500	240°	— 1·489
15	— 1·385	135	— 1·450	255	— 1·512
30	— 1·405	150	— 1·416	270	— 1·535
45	— 1·460	165	— 1·380	285	— 1·510
60	— 1·500	180	— 1·367	300	— 1·492
75	— 1·515	195	— 1·380	315	— 1·458
90	— 1·532	210	— 1·412	330	— 1·395
105	— 1·509	225	— 1·450	345	— 1·382
				360	— 1·372

In Fig. 4 is shown a graph between χ_θ and θ. It will be seen that a curve is obtained verifying relation (5). The values at 90° and 0° are found

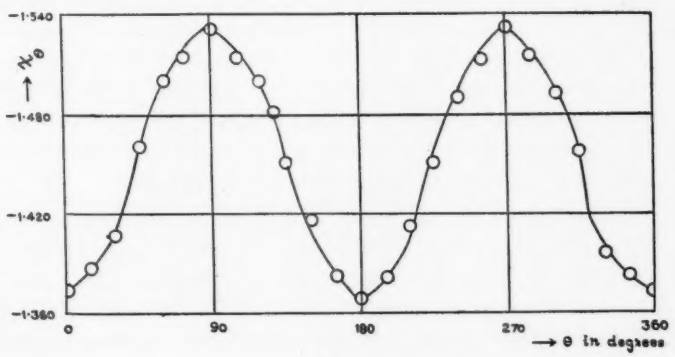

FIG. 4.

to be $-1{\cdot}532$ and $-1{\cdot}372$. It should be mentioned that the zero of the angle θ was chosen to coincide with the position at which χ_θ was a minimum.

The crystal is now placed in each of these positions and the Guoy forces at different field strengths ranging from about $7{\cdot}5$ to about $18{\cdot}5$ kilogauss are determined.

Fig. 5 shows the graphs between χ and $1/H$. On extrapolation the graphs yield for the susceptibility at infinite field strengths the values $\chi_{90} = -1{\cdot}582$ and $\chi_0 = -1{\cdot}422$. It will be noticed that the iron content is fairly small when compared with the values for polycrystalline specimen (see Part I). This is suggestive and one is led to infer that successive meltings and castings reduce such impurities rapidly. The single crystals, as was mentioned earlier, were prepared by melting down the polycrystalline rods and it is likely that the ferromagnetic impurities have decreased considerably.

Since $\chi_{90} = \chi_\perp$ and $\chi_\parallel = \dfrac{\chi_0 - \chi_{90}\cos^2\phi}{\sin^2\phi}$

we calculate the values

$\chi_\perp = -1{\cdot}582$ and $\chi_\parallel = -1{\cdot}160$.

The ratio $\chi_\perp/\chi_\parallel = 1{\cdot}364$.

These values are somewhat larger than those of Focke[16] who gets at 21° C. $\chi_\perp = -(1{\cdot}482 \pm 0{\cdot}014)$ and $\chi_\parallel = -(1{\cdot}053 \pm 0{\cdot}010)$ and the ratio $\chi_\perp/\chi_\parallel = 1{\cdot}408$.

The calculated value for an ideal polycrystalline aggregate in this investigation works to $-1{\cdot}441$ as against Focke's value of $-(1{\cdot}340 \pm 0{\cdot}013)$.

It is well known that small stresses produce proportionately larger strains in single crystals than in polycrystals.[17] The density of the bismuth crystals prepared in the above investigation was $9{\cdot}805$. This value is slightly greater than the mean value of $9{\cdot}795$ for the polycrystalline bismuth rods prepared in Part I. Cold-working at moderate stresses was found to produce very little alteration in density.[18] In fact in the crystals studied here of diameter about 5 mm., the application of a tensional force of 6 kilograms produced an extension of nearly 3 mm. in a rod of length 15 cm. This increase in length produced practically no change in density; in fact, the density of the cold-worked specimen was found to be $9{\cdot}803$.

The stresses applied to the crystal had to be so regulated in magnitude that the strains produced were large enough to produce magnetic alterations but not too large to bring about cosiderable deformation. After cold-working the crystals were investigated magnetically and the principal susceptibilities determined as outlined earlier. The results for a specimen crystal whose ϕ was 34° 30′ are given in Table II below.

TABLE II.

Weight in kg.	$\frac{\delta L}{L}$	Density	Stress $\perp$ kg./cm.^{2}	Stress $\parallel$ kg./cm.^{2}	$\chi_\perp$	$\chi_\parallel$	$\chi_\perp/\chi_\parallel$	Mean χ
0	0·000	9·805	0·00	0·00	− 1·577	− 1·157	1·363	− 1·437
2	0·004	9·805	5·69	8·26	− 1·567	− 1·148	1·365	− 1·427
3	0·007	9·803	8·52	12·39	− 1·523	− 1·097	1·388	− 1·381
4	0·009	9·804	11·36	16·52	− 1·480	− 1·065	1·390	− 1·342
5	0·013	9·804	14·20	20·65	− 1·411	− 1·042	1·354	− 1·288
6	0·018	9·803	17·03	24·79	− 1·382	− 1·034	1·336	− 1·266

It will be noticed that the principal susceptibilities decrease on cold-working. On the other hand, the magnetic anisotropy $\chi_\perp/\chi_\parallel$ at first increases and then after attaining a maximum value shows a gradual decrease. It is possible to account for this variation in a qualitative manner if we remember that when bismuth solidifies from the molten state, there is an increase in volume. This change at the melting point is sometimes responsible for cracking the glass tube during cooling and sufficiently strong glass tubes have to be used to withstand the strain. When therefore the metal is cooled, the glass sides give a lateral strain preventing the metal from expanding as it solidifies. This large strain is perhaps responsible for the larger susceptibility value and the lower magnetic anisotropy obtained here in comparison with the results of Focke. When, therefore, the strain is partly released by cold-working, the anisotropy rises to the normal value and subsequent stresses decrease the anisotropy. The maximum value of this anisotropy 1·390 agrees favourably with Focke's value of 1·408.

The susceptibility of a polycrystalline aggregate as calculated from the data of unstrained crystals is −1·441 while experimental investigations with polycrystals in Part I yield a value of − 1·412. From the well-known views regarding the structure of polycrystals, it seems likely that it would be inappropriate to use the relation $\chi = \frac{1}{3}(2\chi_\perp + \chi_\parallel)$ to determine the susceptibility of polycrystalline metal. This relation at best can give only the approximate value since no account is taken of the slip planes between the small metal crystals in polycrystalline rods and the possible existence of amorphous matter in these regions.

If we agree that the strains produced during solidification are released when the anisotropy reaches the value of 1·390, the mean susceptibility

value of an ideal polycrystalline aggregate is found to be $-1{\cdot}342$ which agrees with Focke's value of $-(1{\cdot}340 \pm 0{\cdot}013)$.

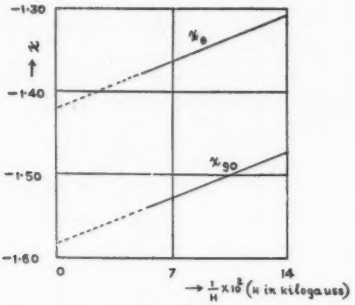

FIG. 5.

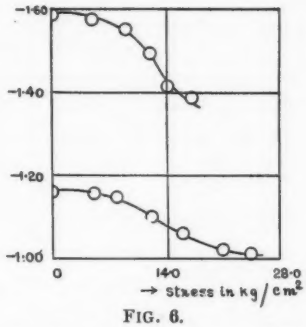

FIG. 6.

In Fig. 6 are drawn graphs between the stresses and susceptibilities parallel and normal to the hexagonal axis. The influence of stress normal to the *c*-axis on the susceptibility in this direction seems to be greater than the corresponding influence in a normal direction. This point will be dealt with later in Section 4.

(*b*) *Zinc.*—The impurities were found to be lead (less than 0·001%) and cadmium (less than 0·001%). Single crystals of this metal are of considerable interest since measurements on their distortion have been made by Mark, Polanyi and Schmid.[19] The crystals produced were brittle and

TABLE III.

θ	χ_θ	θ	χ_θ	θ	χ_θ
0°	− 0·161	120°	− 0·151	240°	− 0·152
15	− 0·160	135	− 0·156	255	− 0·150
30	− 0·157	150	− 0·159	270	− 0·147
45	− 0·154	165	− 0·161	285	− 0·147
60	− 0·150	180	− 0·162	300	− 0·152
75	− 0·148	195	− 0·159	315	− 0·155
90	− 0·147	210	− 0·157	330	− 0·160
105	− 0·148	225	− 0·155	345	− 0·161
				360	− 0·162

the angle between the basal plane and the cylindrical axis could be measured by breaking the crystal. On gradually increasing the tensional force, it is found that at a sufficiently large value well-marked slip bands appeared on the surface. The above authors showed that the linear extension of the crystal could be solely explained by the existence of slip on the basal plane.

In these investigations, the zinc crystals were prepared to have diameters of 2 mm. or 4 mm. approximately. In a few of the thinner crystals, the slip bands appeared when the tensional force was raised to 0·75 kg. The tension was then increased to nearly four times to this value and the measurements were taken. The extensions were so small that variations of the angle ϕ could be neglected.[20] The results obtained at various orientations of an unstrained crystal whose ϕ was 31° 5′ are given in Table III.

The graph between χ_θ and θ is shown in Fig. 7. The maximum and minimum values of the susceptibilities are found from the graph to be

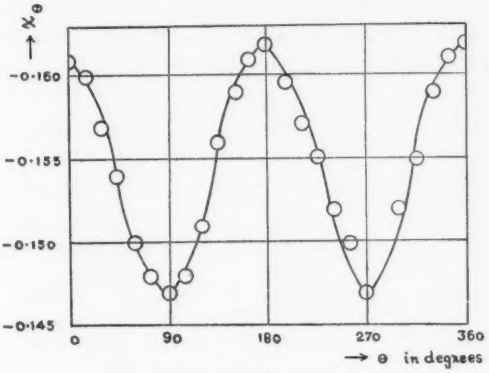

FIG. 7.

$-0·162$ and $-0·147$ respectively. The crystal was next placed at these orientations and the Guoy forces were determined for different field strengths

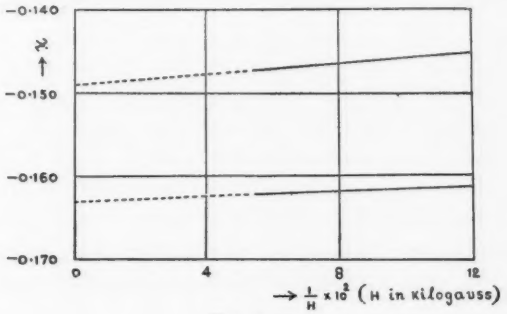

FIG. 8.

(Fig. 8). On extrapolation of the 1/H curves, the susceptibility values at infinite field strengths were found to be $\chi_0 = -0{\cdot}163$ and

$\chi_{90} = -0{\cdot}149$. On calculation these values give

$\chi_\perp = -0{\cdot}149$

and

$\chi_\parallel = -0{\cdot}202$.

The ratio $\chi_\parallel/\chi_\perp$ or the magnetic anisotropy has the value 1·356 and the susceptibility of a polycrystalline aggregate as calculated from the relation

$\chi = \frac{1}{3}[2\chi_\perp + \chi_\parallel]$ works to $-0{\cdot}167$.

These results compare favourably with those of McLennan, Ruedy and Cohen[5] who report the following values :—

$\chi_\parallel = -0{\cdot}190$, $\chi_\perp = -0{\cdot}145$, $\chi_\parallel/\chi_\perp = 1{\cdot}310$,

and $\chi = -0{\cdot}160$.

The following table gives the variations of the principal susceptibilities as the zinc crystals were subjected to cold-working.

TABLE IV.

$\frac{\delta L}{L}$	Rel. Density ρ	$\chi_\perp$	$\chi_\parallel$	$\chi_\parallel/\chi_\perp$	Mean χ
0·000	7·132	− 0·149	− 0·202	1·356	− 0·167
0·006	7·132	− 0·149	− 0·200	1·342	− 0·166
0·009	7·131	− 0·148	− 0·200	1·351	− 0·165
0·014	7·131	− 0·149	− 0·200	1·342	− 0·166
0·019	7·131	− 0·147	− 0·198	1·347	− 0·164

A scrutiny of the above table shows that the principal susceptibilities alter very little on cold-working. The magnetic anisotropy is almost constant and the mean susceptibility of the polycrystalline aggregate also tends to be constant. The effect of cold-working seems to be small in the case of zinc crystals. If at all a change can be inferred, the values seem to show a small decrease as the stress is raised sufficiently.

Polycrystalline zinc showed a definite though small decrease in susceptibility but it will be remembered that the density altered appreciably in those investigations.

Considering the fact that the principal susceptibilities vary very little with cold-working, it may be safely assumed that the stress effects that arise during the solidification of the molten metal in the process of crystallisation do not affect appreciably the susceptibility values.

(*c*) *Tin.*—The impurities in this metal were found to be copper (less than 0·001%) and lead (less than 0·01% and nearer 0·001%). Single crystals of tin are formed more easily than bismuth or zinc. The difficulty in investigations on tin arises from the small magnitude of its susceptibility. Since no special arrangement was devised to grow tin crystals with a specific orientation, many of the crystals prepared had the tetragonal axis coincident with the cylindrical axis. A few crystals however had small ϕ values. This angle was found to be always smaller than 5°. The orientations could be measured by an adaptation of the Bridgman's method accurately to 1′ of arc.

The measurements of the Guoy forces were made with the crystals which had small ϕ values at different positions with respect to the magnetic field. The alterations of the Guoy forces as θ was varied from 0° to 360° was very small. In one of the crystals for which $\phi = 4° 32'$, the maximum Guoy force was 12 mg. while the minimum was 11·6 mg. weight. The corrected susceptibility value for these orientations lead to a calculation of the principal paramagnetic susceptibilities. The mean of a number of measurements with different crystals gave the following values :—

$$\chi_{\perp} = 0{\cdot}0400 \pm 0{\cdot}0009$$

$$\chi_{\parallel} = 0{\cdot}0387 \pm 0{\cdot}0008$$

$$\chi_{\perp}/\chi_{\parallel} = 1{\cdot}034.$$

The susceptibility of an ideal polycrystalline aggregate is given by the relation $\chi = \frac{1}{3}[2\chi_{\perp} + \chi_{\parallel}]$ works to $0{\cdot}0396 \pm 0{\cdot}0009$.

Hoge's results give $\chi_{\perp} = 0{\cdot}0270$; $\chi_{\parallel} = 0{\cdot}02441$.

$$\chi_{\perp}/\chi_{\parallel} = 1{\cdot}120 \text{ ; Mean } \chi = 0{\cdot}0259.$$

There is satisfactory agreement between these sets of values particularly when it is remembered that Hoge's crystals were grown in graphite moulds of square section while the crystals in the present investigation have been prepared in glass tubes.

The density of the crystals was found to be 7·288 as against the value of 7·262 obtained for polycrystals. The effect of cold-working on the single crystals is illustrated by the following table. The crystal used had $\phi = 4° 30'$.

TABLE V.

$\frac{\delta L}{L}$	Rel. Density ρ	$\chi_\perp$	$\chi_\parallel$	$\chi_\perp/\chi_\parallel$	Mean χ
0·000	7·288	0·0402	0·0389	1·033	0·0398
0·005	7·286	0·0398	0·0380	1·047	0·0392
0·009	7·285	0·0395	0·0372	1·062	0·0387
0·016	7·282	0·0393	0·0360	1·092	0·0382
0·023	7·280	0·0392	0·0352	1·114	0·0345
0·035	7·278	0·0391	0·0341	1·147	0·0341

The principal susceptibilities and their ratio are plotted against the extension in Fig. 9. While $\chi_\perp$ decreases by a small amount, $\chi_\parallel$ is found to show a much larger dimunution. This is obvious since the tetragonal axis makes a small angle with the cylindrical axis and hence the effects are greater in a direction parallel to the tetragonal axis. The ratio $\chi_\perp/\chi_\parallel$ gradually

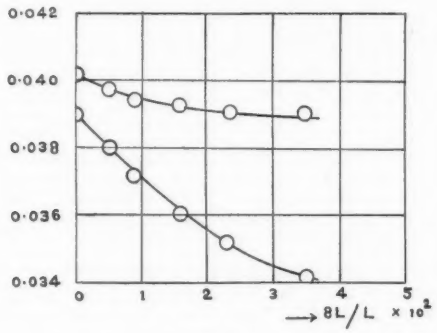

FIG. 9.

increases as the tensional stress is increased. The mean susceptibility shows a gradual decrease.

A calculation of the stress normal and parallel to the tetragonal axis was made in the above cases, but since the normal stresses were small, no definite conclusions could be drawn. The results of the application of stress

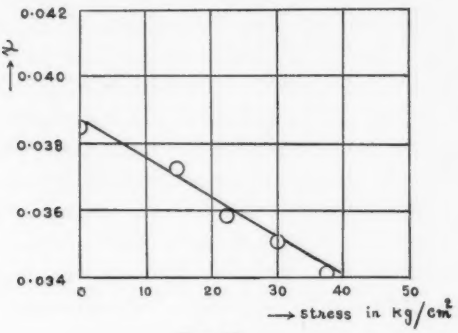

FIG. 10.

on a tin crystal whose tetragonal axis coincided with the cylindrical axis are given below. The diameter of the crystal was 4·12 mm.

TABLE VI.

Force in kg. wt.	$\frac{\delta L}{L}$	Rel. Density ρ	Stress in kg. wt. per sq. cm.	$\chi_{\parallel}$
0	0·000	7·283	0·0	0·0385
2	0·008	7·281	15·0	0·0373
3	0·014	7·282	22·5	0·0358
4	0·022	7·280	30·0	0·0351
5	0·031	7·281	37·5	0·0341

The above results show that the application of relatively large stresses produce small changes in the paramagnetic susceptibility of white tin. It will be remembered that polycrystalline tin showed larger decrease in susceptibility (and even a change in sign) when stresses of nearly equal magnitude were applied.

4. Discussion.

The three metals studied above seem to represent three different types of magnetic behaviour of metal crystals in relation to cold-working.

Bismuth single crystals show a decrease in the mean susceptibility when cold-worked. The decrease appears to be of about the same order of magnitude as the decrease obtained with polycrystalline bismuth. This is an

interesting result since it suggests that the nature of the distortion produced by stretching polycrystalline bismuth rods is similar to what obtains in single crystals. Considering the susceptibility changes, we have changes due to distortion within the small crystals composing the polycrystal and also changes due to distortion of the matter in the boundaries. The distortion inside the small crystals appears to affect the susceptibility much more than the distortion in the boundary. Our results suggest that the boundary deformation contributes only to a decrease in density and very little to susceptibility variation.

We shall next consider the nature of diamagnetism in bismuth crystals. Ehrenfest[21] and Raman[22] have suggested that the high diamagnetism of bismuth and graphite is due to the presence of large electron orbits. This would suggest that the mean free path of the valency electron is large when compared with the interatomic distances. The susceptibility in any direction would include the contribution by the bismuth ions and the resolved component of the susceptibility due to the valency electrons. The effect of stress in cold-working is to influence the second factor.

A reference to Table II indicates that the susceptibility variation is greater in a direction perpendicular to the *c*-axis than parallel to it. If a stress is applied in any direction in the crystal to produce a small plastic deformation, the susceptibility is likely to be influenced in the direction of the stress and also in a perpendicular direction. The investigations of Goetz and Focke[6] indicate that when the temperature of the crystal is raised, the decrease of diamagnetism is 40% greater perpendicular to the *c*-axis than parallel to it. There is thus a close similarity between the effects due to cold-working and to the raising of temperature. It is also known that the direction of densest packing lies normal to the basal plane while the direction of the least dense packing lies in it. Hence the denser the crowding along a direction, the smaller is the component of the free path in this direction and correspondingly the lower becomes the diamagnetic susceptibility value. This is evidenced by the numerically greater value of $\chi_\perp$ than of $\chi_\parallel$. The effect of producing an elongation in a crystal is to produce some kind of distortion inside the crystal which results in the distortion of the Raman-Ehrenfest orbits.[23]

Considering now the nature of distortion in bismuth crystals, the investigations of several workers show that deformation of the crystal by slip is doubtful. In fact, Mugge[24] and Gough and Cox[25] have reported that in bismuth crystals, the whole of the distortion seems to take place by twin formation. Similar observations have been made by the writer, when crystals subjected to stresses, were broken after the magnetic investigations,

It is difficult to see how a mere twin formation will result in such a large decrease of the mean diamagnetic susceptibility of single crystals, the order of the decrease being the same as in polycrystals. The causes, that bring about the observed decrease in susceptibility, seem to be more fundamental.

There is considerable evidence to indicate the presence of a secondary structure in metals.[26] Zwicky[27] postulates a microcrystal block inside a crystal as a region surrounded by a surface physically different from a similar surface taken within the block. The dimensions of these blocks appear to be of the order of 100 A.U. Such microcrystals seem to be most well-developed in bismuth. On subjecting the crystal to stress, a slip or a distortion on the boundaries of these microcrystals occurs. These considerations receive considerable support from the investigations of Goetz and Focke on bismuth crystals with admixtures of small quantities of foreign matter. But instead of the volume effect due to a superstructure, they introduce a superstructure of planes with a parameter of 10^3 to 10^4 A.U., which is in good agreement with the results of etch figures and the 'critical' size of colloidal powders (below which the susceptibility decreases rapidly on size diminution[28]). This superstructure becomes unstable above 75° C. without the lattice getting affected. There is evidence for this effect from the pseudo-allotropic transformation observed at 75° C.[6] The foreign matter gets absorbed in these planes which act as reflectors for the mobile electrons with large mean free path. The susceptibility is hence affected from the Ehrenfest-Raman point of view. Such superstructure of planes, on the theory of Goetz, should exist both in the single crystals and also in the small crystals within the polycrystal. An examination of the facets developed, when a polycrystalline rod of bismuth was broken, showed under the microscope a dimension of about 1 mm. for these small crystals. In each small crystal, therefore, there may exist a thousand planes of the type contemplated by Goetz. When the crystal, produced by slow cooling, is subjected to stress, it appears that slip may occur along the planes which compose the superstructure and in a direction parallel to that of the applied stress. Such distortions produce deformation of the Ehrenfest-Raman orbits and thus cause a decrease in the diamagnetic susceptibility. In the absence of a definite knowledge of the positions of the superimposed planes, it is difficult to give a quantitative explanation to the observed susceptibility changes along and perpendicular to the *c*-axis.

The case of zinc crystals is somewhat simpler. The atomic susceptibilities in the directions parallel and perpendicular to the *c*-axis are found to be $-13{\cdot}21$ and $-9{\cdot}74$ respectively. The diamagnetism of zinc ions

(Zn^{+2}) according to Kido[29] is $-12\cdot8$ while Pascal[30] gives $-13\cdot5$. These values indicate that the binding parallel to the c-axis is homopolar while normal to it, it is metallic.

The distortion of single crystals of zinc by tensional forces has been studied by Mark, Polanyi and Schmid.[19] Well-marked slip bands appeared on the surface, when the tension became sufficiently large and the inclination of the glide planes to the axis of the rod (or the direction of pull) became smaller. Extension of the rod could be entirely accounted for by means of slip on the basal plane. The effect of stress on a metal with homopolar binding is likely to be small from the magnetic point of view. Where the binding is metallic, the investigations of Honda and Shimizu[2] outlined in Part I suggest a small increase in the diamagnetic susceptibility. But no density changes were observed in the zinc crystals as they were cold-worked. Hence, the increase of diamagnetism on this account should be negligible. The distortion of the orbits, however, should produce a small decrease in susceptibility which is exactly what is observed.

In the case of white tin, the binding is metallic. The valency electrons contribute a large paramagnetism which is independent of temperature. The atomic susceptibility of white tin is $4\cdot7$, while the ionic susceptibility of tin ions (Sn^{+4}) according to Kido[29] is -13. This gives a paramagnetic susceptibility for the four valency electrons of $17\cdot7$ per gram atom. The effect of applying a stress according to the theory of Honda and Shimizu is to decrease the paramagnetic susceptibility by a small amount, when the density decreases appreciably. This is exactly what is observed in Table V.

It will be noted that polycrystalline tin and single crystals of tin differ in their magnetic properties in relation to stress effects. The density and susceptibility variations are much greater with polycrystals than for single crystal specimens. This indicates that the effects in the boundaries of the small crystals inside the polycrystalline tin are more predominant than in single crystals. This may account for the well-known malleability of tin.

5. *Summary.*

Single crystals of bismuth, zinc and tin were prepared by the method of slow cooling and the influence of cold-working on the principal susceptibilities was investigated. Bismuth crystals showed a decrease in susceptibility, this decrease being of the same order of magnitude as what is obtained in polycrystals. This has been explained by assuming a superstructure of planes after Goetz and Focke. Zinc crystals showed very small decrease in the diamagnetic susceptibility on cold-working. Tin crystals had their paramagnetic susceptibility slightly lowered by tensional stress. This decrease

was much smaller than what was obtained in polycrystals. This has been accounted for as being due to the greater influence of the *boundaries* of the small crystals (inside the polycrystal) than the *interior*. The theory of Honda and Shimizu adequately explains these observed changes of susceptibility.

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THE RAMAN SPECTRA OF TRI-METHYL-AMINE AND SOME COMPOUNDS OF HYDROXYLAMINE AND HYDRAZINE.

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1. *Introduction.*

The importance of a detailed study of the Raman spectra of comparatively simple molecules has been pointed out by the author in earlier communications to these *Proceedings*.[1] In the present paper, the Raman spectra of $N(CH_3)_3$, $NH_2OH.HCl$, $(NH_2OH)_2.H_2SO_4$, $HCl.N_2H_4.HCl$ and $N_2H_4.H_2O$ are reported on, and discussed in some detail.

2. *Experimental.*

10 grams of tri-methyl-amine (Kahlbaum, 'wasserfrei') distilled in vacuum was employed in the investigation. The hydrochloride and hydrosulphate of hydroxylamine were studied in the crystalline state as well as in concentrated aqueous solution. In the case of hydrazine, the hydrochloride and a 50% solution of the hydrate were examined. A Hilger two-prism spectrograph was used for photographing the spectrum in the case of trimethyl-amine; a Fuess spectrograph of somewhat higher dispersion was employed for the rest of the work.

[1] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 527; **4**, 74, 82.

3. *Results.*

TABLE I.

Raman spectrum of tri-methyl-amine: $N(CH_3)_3$.

No.	ν	Assignment	Int.	ρ	No.	ν	Assignment	Int.	ρ
1	19960	*e*—2978	2*b*	D	20	22564	*e*—374	2	P
2	19987	*e*—2951	4	P	21	22663	*e*—275	2*bd*	D
3	20110	*e*—2828	2	P	22	23236	*k*—1469	3	D
4	20166	*e*—2772	6	P	23	23267	*k*—1438	3	D
5	20200	*e*—2738	0	P	24	23299	*k*—1406	1	D
6	21464	*e*—1474	3	D	25	23425	*k*—1280	0*d*	D
7	21494	*e*—1444	3	D	26	23518	*k*—1187	3*s*	P
8	21536	*e*—1402 } *i*—2980 }	1	D	27	23663	*k*—1402	2*b*	D
					28	23878	*k*—827	4*s*	P
9	21572	*i*—2924	1	P	29	24282	*k*—423	1*d*	D
10	21658	*e*—1280	0*bd*	D?	30	24407	*p*—2946 } *q*—2981 }	4*b*	P
11	21729	*k*—2976	6*b*	D					
12	21756	*e*—1182 } *k*—2949 }	10*b*	P	31	24443	*q*—2945	5*b*	P
					32	24473	*o*—2820	1*d*	P
13	21785	*k*—2920 ?	0*d*	?		24516	*o*—2777	—	—
14	21884	*k*—2821	8	P		(Hg)	*p*—2837		
15	21934	*k*—2771	12	P	34	24535	*p*—2818	1*d*	P
16	21969	*k*—2738	3	P	35	24570	*q*—2818	2	P
17	22109	*e*—829	6*s*	P	36	24591	*p*—2762	2	P
18	22206	*k*—2499 ?	0*bd*	D	37	24628	*p*—2725 } *q*—2760 }	6	P
19	22510	*e*—428	2*b*	D					

$\Delta\nu$ (cm.$^{-1}$).	275	374	428	828	1042	1187	1280	1404	1442	1472
Int. ..	2*bd*	2	2*b*	6*s*	2*b*	3*s*	0*d*	1	3	3
ρ ..	D	P	D	P	D	P	D	D	D	D

$\Delta\nu$ (cm.$^{-1}$).	2499?	2738	2770	2820	2920?	2948	2978
Int. ..	*Obd*	2	12	8	0*d*	10*b*	6*bd*
ρ ..	D	P	P	P	?	P	D

TABLE II.

Raman spectra of $NH_2OH.HCl$ and $(NH_2OH)_2.H_2SO_4$.

$NH_2OH.HCl$		$(NH_2OH)_2.H_2SO_4$	
Crystal	$\Delta\nu$ = 1000·5 cm.$^{-1}$ (3*s*)	*Aq. solution*	$\Delta\nu$ = 450 (5*b*)
Aq. solution	$\Delta\nu$ = 1008 cm.$^{-1}$ (6)		624 (4*b*)
	2962 (2*b*)		982 (10)
	Water 3227 (1*b*)		1008 (8)
	Water 3435 (6*vb*)		1112 (2*b*)
	Water 3620 (1*b*)		2987 (1*b*)
			Water 3227 (1*b*)
			Water 3435 (6*vb*)
			Water 3620 (1*b*)

TABLE III.

Raman spectra of $HCl.N_2H_4.HCl$ and $N_2H_4.H_2O$.

$HCl.N_2H_4.HCl$		$N_2H_4.H_2O$	
Crystal	$\Delta\nu$ = 1024 cm.$^{-1}$ (1*s*)	50% *solution*	$\Delta\nu$ = 916 (0*d*)
			1126 (1)
Aq. solution	$\Delta\nu$ = 967 (1)		3215 (½)
	1029 (3)		3286 (3)
	1108 (½*d*)		3350 (2)
	3190 (1*d*)		
Water	3284 (½*d*)		
	3432 (6*vb*)		
	3640 (1*b*)		

4. Discussion of Results.

1. *Tri-methyl-amine*: $N(CH_3)_3$.—So far as the author is aware,[2] the Raman spectrum of tri-methyl-amine has been studied only by Dadieu and Kohlrausch.[3] As the following table will show, their results are very incomplete.

TABLE IV.

Dadieu-Kohlrauch	Author		
$\Delta\nu$ (Int.)	$\Delta\nu$	Int.	ρ
	275	2*bd*	D
	374	2	P
	428	2*b*	D
826 (1)	828	6*s*	P
	1042	2*b*	D
1182 (½)	1187	3*s*	P
	1280	0*d*	D
1439 (0)	1404	1	D
	1442	3	D
	1472	3	D
	2499?	0*bd*	D
2770 (3)	2738	2	P
	2820	8	P
	2920?	0*d*	?
2942 (3*br*)	2948	10*b*	P
2977 (1*br*)	2978	6*bd*	D

A noteworthy feature of the Raman spectrum of this substance is the extreme feebleness of the rotational wings accompanying the Rayleigh lines.

[2] *See* J. Weiler, "Raman Effekt," *Landolt-Börnstein Tabellen*, 1935, p. 1026.

[3] A. Dadieu and K. W. F. Kohlrausch, *Wien. Bericht.*, 1930, **139**, 459.

This suggests that the optical anisotropy of the molecule is very small so that the depolarisation of the Rayleigh scattering for the liquid as well as for the vapour might be expected to be comparatively low.

If we confine our attention to the frequencies below 1100 cm.$^{-1}$ then, as a first approximation we can disregard the H atoms and treat the molecule of tri-methyl-amine as the general AB_3 type having the symmetry C_{3v}. In the region with which we are concerned, there are five Raman lines of which two are polarised, and three depolarised. This is rather surprising, since the model in question has only four distinct frequencies, two, totally symmetric ($\rho \ll \frac{6}{7}$) and two doubly degenerate ($\rho = \frac{6}{7}$). From a comparison with the Raman spctrum of iso-butane, H.C $(CH_3)_3$ which has been recently discussed by the author[4] we are led to the following classification of the observed frequencies :

Substance	Totally symmetric		Doubly degenerate	
	$\nu_1(CH_3)$	$\delta_3(CH_3)$	$\nu_{2,3}(CH_3)$	$\delta_{1,2}(CH_3)$
$H \cdot C(CH_3)_3$ ..	795 (10) P	437 (1) P	965 (4*b*) D	370 (4*b*) D
$N(CH_3)_3$ ..	828 (6*s*) P	374 (2) P	1042 (2*b*) D	428 (2*b*) D

This leaves the broad and depolarised Raman band at 275 cm.$^{-1}$ unexplained. This band appears to be quite analogous to the low frequency Raman band observed by the author in the spectra of liquid H_2O and D_2O[5]. A similar intense depolarised Raman band at about 200 cm.$^{-1}$ has been observed in the case of liquid formic acid. These bands owe their origin, perhaps, to the hindered rotation of the liquid molecules, but their presence in certain cases and absence in others is rather difficult to understand.

The fact that the assignment of the frequencies of iso-butane given by Kohlrausch is incorrect in view of the author's polarisation measurements has been pointed out in a previous communication.[6] It follows therefore that the calculations of Kohlrausch and Köppl[7] in the case of iso-butane are not significant.

[4] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1936, 3, 527.

[5] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1935, 2, 291; 1936, 3, 201.

[6] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1936, 3, 527.

[7] K. W. F. Kohlrausch and F. Köppl, *Z. f. Phys. Chem.*, B, 1934, 4, 630.

Howard and Wilson[8] have discussed the normal frequencies of vibration of the symmetrical pyramidal molecule AB_3 using a general potential energy function involving six constants. The central force system adopted by Dennison,[9] and the valence force system employed by Lechner[10] involve two constants and give identical expressions for the ratio $\left(\frac{\omega_1\omega_2}{\omega_3\omega_4}\right)^2$ where ω_1 and ω_2 are the totally symmetric and ω_3 and ω_4 the doubly degenerate frequencies of the AB_3 molecule. From this ratio, it is possible to make an estimate of the angle β between the edge and the height of the pyramid. A rough computation (neglecting the H atoms) gives $\beta = 62° 30'$ in the case of iso-butane, and $\beta = 70° 16'$ in the case of N $(CH_3)_3$. If the carbon valencies in iso-butane are assumed to be tetrahedral, we should find $\beta = 70° 32'$. The fact that the carbon valencies in saturated compounds tend to preserve at least approximately, the tetrahedral structure is supported by chemical evidence as well as by evidence derived from electron diffraction experiments. The large deviation of the calculated value from the expected one is therefore to be ascribed to the fact that neither the central nor the valence force system is applicable for the present case. Indeed, Howard and Wilson[11] as well as Redlich and Pordes[12] have found that even in the case of very simple molecules such as the tri-halides, $CHCl_3$, $CDCl_3$, etc., the central force system and the valence force system are equally unsatisfactory.

A characteristic difference between the Raman spectra of H.C $(CH_3)_3$ and N $(CH_3)_3$ revealed by the polarisation photographs is the striking reversal in the state of polarisation of the two lowest fundamental frequencies (370 and 437 in the case of iso-butane and 374 and 428 in the case of tri-methyl-amine). In the spectrum of iso-butane, the frequency $\Delta\nu = 370$ is depolarised and $\Delta\nu = 437$ polarised, whereas in the spectrum of tri-methyl-amine $\Delta\nu = 374$ is polarised and $\Delta\nu = 428$ is depolarised.

In the frequency interval between 1100 cm.$^{-1}$ and 1500 cm.$^{-1}$ we find marked differences between the spectra of tri-methyl-amine and iso-butane as will be seen from the table below.

The splitting of the 1450 Raman band which arises from the δ (C–H) vibration of the CH_3 groups into three components is very exceptional, and is therefore a significant feature of the Raman spectrum of tri-methyl-amine.

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[8] J. B. Howard and E. B. Wilson, *Jour. Chem. Phys.*, 1934, **4**, 630.

[9] D. M. Dennison, *Phil. Mag.*, 1926, **1**, 195.

[10] F. Lechner, *Wien. Bericht.*, 1932, **141**, 633.

[11] J. B. Howard and E. B. Wilson, *Loc. cit.*

[12] O. Redlich and F. Pordes, *Monat. f. Chem.*, 1936, **67**, 203.

$H.C(CH_3)_3$	$\Delta\nu$	1170		1325		1452	
	Int.	4*b*		3*b*		7*b*	
	ρ	D		D		D	
$N(CH_3)_3$	$\Delta\nu$	1187	1210		1404	1442	1472
	Int.	3*s*	0*d*		1	3	3
	ρ	P	D		D	D	D

2. *Hydroxylamine hydrochloride and sulphate*: $NH_2\ OH.\ HCl$, $(NH_2\ OH)_2.\ H_2SO_4$.—The Raman spectrum of pure NH_2OH (liquid) has been studied by Medard[13] who has found the following frequencies[14]:

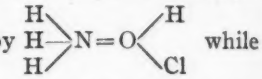
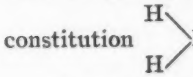
$\Delta\nu$ ..	897	921	1045	1108	1311	1605	3259	3306
Int. ..	6	6	0	1	0	3	5	3

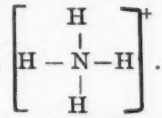
He has remarked that due to the rapid decomposition of the substance with evolution of bubbles, the spectrum obtained was quite mediocre. It is rather surprising that neither of the two strong lines 897 and 921 is observed in the Raman spectra of the salts investigated by the present author. The Raman spectrum of crystalline $NH_2OH.HCl$ consists of a single sharp line with a frequency shift of 1000·5 cm.$^{-1}$ In solution, this line is slightly shifted towards the longer wave-length side ($\Delta\nu = 1008$) but remais still the strongest line in the spectrum. This line occurs with equal prominence in the aqueous solution of the sulphate, and is well polarised in both cases. Besides, the aqueous solution of the hydrochloride shows a band extending over about 60 wavenumbers and with its centre at 2962 cm.$^{-1}$ The water bands are, of course, a prominent feature of the spectra of the aqueous solutions, but there is a considerable strengthening of the central component of the band—which extends roughly over 150 wave-numbers—due, no doubt, to the superposition of the O–H and N–H vibrations of NH_2OH. Besides the Raman bands referred to above, the aqueous solution of the sulphate shows also the Raman frequencies 450 (5*b*), 624 (4*b*), 982 (10), and 1112 (2*b*) which are the characteristic frequencies of the tetrahedral (SO_4) ion.

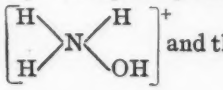
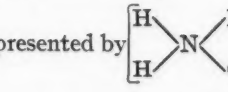
From the chemical standpoint, the constitution of hydroxylamine is a problem of some interest. If, as is generally accepted, hydroxylamine is thought of as being derived from ammonia by the substitution of one of the H atoms by the hydroxyl group (OH), then the constitutional formula of hydroxylamine will be represented by $H_2 = N - OH$, the nitrogen being

[13] L. Medard, *C. R.*, 1934, **199**, 421.

[14] *See* J. Weiler, "Raman Effekt," *Landolt-Börnstein-Tabellen*, 1935, p. 949.

trivalent. While this is in conformity with the larger body of chemical evidence, there are certain cases where the behaviour of hydroxylamine appears to accord better with the constitution $H_3 \equiv N = O$, the nitrogen being pentavalent. "In alkaline solutions, hydroxylamine plays the rôle of an amido-acid $H_2 = N - OH$, and acts as a reducing agent, while in acid solutions, it behaves like ammonia oxide $H_3 \equiv N = O$, and acts as an oxidising agent.[15]" According to this view, the structure of a salt of hydroxylamine, say, the hydrochloride will be represented by  while sodium hydroxylamate in which NH_2OH functions as an acid will have the constitution  .

It is interesting to point out the relation between tri- and quinqevalent nitrogen on the basis of the electronic theory of valency.[16] Nitrogen (atomic number 7) has five valency electrons and so can complete its octet by taking up three hydrogen atoms. Thus in ammonia, NH_3, there are six shared electrons, and two unshared. If a fourth neutral H atom were taken up, this would introduce another electron and the valency group would consist of nine, as it does in sodium (2, 8, 1). Hence neutral NH_4 behaves like a univalent metal. The valency group is, however, very unstable. It readily loses one electron, and forms the stable ammonium ion  . This explains why that one of the five valencies of pentavalent nitrogen must always be an electrovalency. A nitrogen atom which has lost one electron (N^+) behaves like tetravalent carbon. The fifth group, the anion, is not attached to the ammonium ion in any fixed position, but is merely attracted to it as a whole.

If we extend the ammonium group theory to hydroxylamine, the hydroxylammonium ion will be represented by  and the salt of hydroxylamine, say, the hydrochloride will be represented by  ,

[15] *See* J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 1928, **8**, 297.

[16] N. V. Sidgwick, *The Electronic Theory of Valency*, 1927, 65.

where X stands for the anion. Since ionic bindings do not give Raman effect, we should expect, the anion and the cation to give their own characteristic frequencies. This is in fact what is actually observed. The characteristic Raman lines at 1000·5 and 1008 cm.$^{-1}$ observed respectively in the spectra of the crystal and aqueous solution of the salts of hydroxylamine arise no doubt from the mutual vibration of the N and O atoms of the $\left[\begin{matrix}H\\H\!\!>\!\!N-OH\\H\end{matrix}\right]^+$ ion. Indeed, on the analogy between C and N^+ we can compare this Raman line to the intense line at 1035 cm.$^{-1}$ observed in the Raman spectrum of methyl alcohol, $\begin{matrix}H\\H\!\!>\!\!C-OH\\H\end{matrix}$. If as a rough approximation we ignore the H atoms and consider the hydroxylammonium ion as a diatomic N–O, we get for the force constant (putting $\Delta\nu = 1008$) $f = 4{\cdot}45 \times 10^5$ dynes/cm.

The complete elucidation of the frequencies in the 3 μ region is of great interest in the case of the $\left[\begin{matrix}&H&\\H&-N-&H\\&H&\end{matrix}\right]^+$ and $\left[\begin{matrix}H\\H\!\!>\!\!N-OH\\H\end{matrix}\right]^+$ ions in view of the analogy with the corresponding carbon compounds. The great intensity of the water bands which fall practically in the same region renders the matter one of extreme difficulty in the case of aqueous solutions. The use of heavy water as solvent would obviate this difficulty, and the author hopes beforelong to take up this problem.

(3) *Hydrazine hydrochloride and Hydrazine hydrate*: *HCl.N_2H_4.HCl*, *$N_2H_4.H_2O$*.—The Raman spectrum of pure hydrazine as well as that of the pure hydrate has been studied by Imanishi.[17] Aqueous solutions of the hydrate have been studied by Pal and Sen Gupta.[18] The spectra of the pure susbtance and of the hydrate do not seem to differ appreciably. The author's results for the hydrate are in fair agreement with those of the previous workers.

The spectrum of hydrazine hydrochloride in the crystalline state shows a single sharp line at 1024 cm.$^{-1}$ In the aqueous solution this line is the most prominent and is shifted by about 5 wavenumbers to the longer wavelength side. Besides, two fainter lines are also observed in the aqueous solution, one at 967 and the other at 1108 cm.$^{-1}$ The 3 μ region shows certain details as will be seen from Table III, but the use of heavy water as

[17] S. Imanishi, *Sci. Pap. Inst. Phys. Chem. Res.*, 1931, **16**, 1.

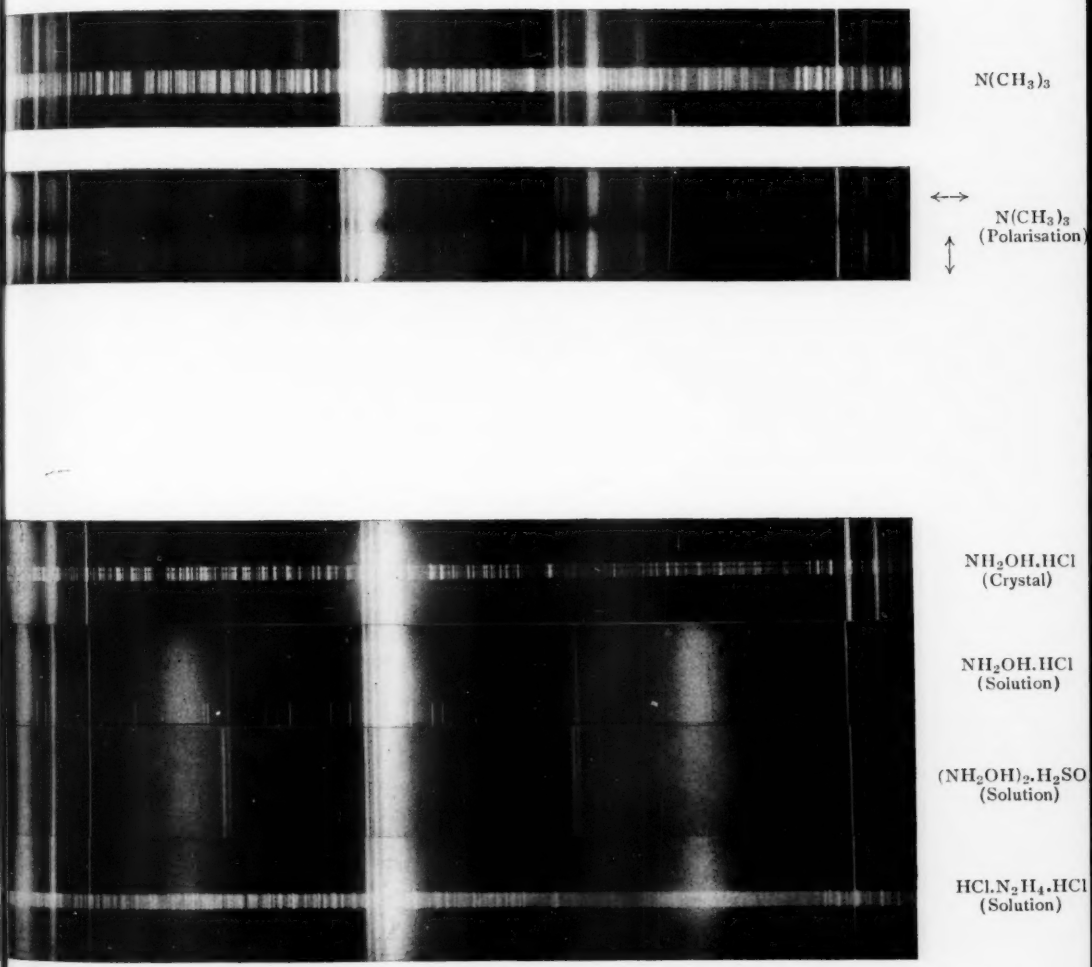
[18] N. N. Pal and P. N. Sen Gupta, *Ind. Jour. Phys.*, 1930, **5**, 13.

solvent might be expected to show many new features. The configuration of $HCl.N_2H_4.HCl$ can be written as $\overline{Cl}\left[\begin{matrix}H\\H\\H\end{matrix}\!\!>\!N-N\!<\!\!\begin{matrix}H\\H\\H\end{matrix}\right]^{++}\overline{Cl}$ so that the vibrations of the hydrazinium ion should be somewhat analogous to those of ethane, $\begin{matrix}H\\H\\H\end{matrix}\!\!>\!C-C\!<\!\!\begin{matrix}H\\H\\H\end{matrix}$. It may not be wrong to compare the Raman line $\Delta\nu = 1029$ of the hydrazinium ion to the strong Raman line 992 of ethane. A rough computation gives for the magnitude of the N–N force constant, $f = 4{\cdot}35 \times 10^5$ dynes/cm.

In conclusion, the author wishes to express his respectful thanks to Professor Sir C. V. Raman for his kind interest in the present work.

5. *Summary.*

The Raman spectrum of tri-methyl-amine has been investigated and the observed frequencies are discussed with the aid of polarisation data. Certain conclusions regarding the proper assignment of the frequencies have been drawn from a comparison with the spectrum of iso-butane which has been investigated on a former occasion. The hydrochlorides of hydroxylamine and hydrazine show but a single Raman line in the crystalline state. This line remains quite strong even in aqueous solutions, but the latter also show certain additional features. The constitution of these salts is discussed on the basis of the electronic theory of valency ; the conclusions drawn therefrom seem to be supported by the Raman effect.



Raman Spectra

ULTRASONIC VELOCITIES IN ORGANIC LIQUIDS.

Part VI. Related Compounds.

By S. Parthasarathy.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received August 14, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

In a series of papers, the author gave determinations of acoustic velocity in a variety of organic compounds and discussed the relation between sound velocity and chemical constitution. The work has been further extended in this paper wherein some esters, nitro-compounds, two aldehydes and two oils have been experimented upon.

The same experimental arrangement as that used in previous work has been employed, both for production of ultrasonic waves and for photographing the diffraction spectra produced by them.

The frequency of vibration of the quartz plate was measured for every liquid by means of a wave-meter and the wave-length of sound in the liquid was calculated by the well-known formula. The frequency employed was about $7 \cdot 32 \times 10^6$ c./s.

The purest liquids were employed after distillation. They were mostly of Kahlbaum stock, Merck's being employed where the former were not available.

2. Results.

Table I gives the velocities with adiabatic compressibilities calculated therefrom for the various liquids investigated.

Previous determination of sound velocity is available for only *o*-nitrotoluene and it is given for comparison in Table II.

TABLE I.

Ultrasonic velocities in organic liquids at $7 \cdot 32 \times 10^6$ *c./s. nearly.*

	Liquids	Chemical Formula	Temp. in °C.	Density	Velocity of sound in metres/second	Adiabatic Compressibility $\beta\phi \times 10^6$
1	Ethyl carbonate	$CO(OC_2H_5)_2$	28°	0·977	1173	74·4
2	Ethyl caprylate	$CH_3(CH_2)_6.COOC_2H_5$	28°	0·872	1263	71·9
3	Methyl salicylate	$OH.C_6H_4.COOCH_3$	28°	1·189	1408	42·8
4	Geranyl acetate	$C_{12}H_{20}O_2$	28°	0·915	1328	61·9
5	Nitro-toluene-*o*	$CH_3.C_6H_4.NO_2$	28°	1·168	1451	40·7
6	Nitro-toluene-*m*	,, ,,	28°	1·162	1451	40·9
7	Nitrobenzene	$C_6H_5 \cdot NO_2$	28°	1·198	1455	39·4
8	Salicylaldehyde	$OH.C_6H_4.CHO$	27°	1·166	1474	39·5
9	Citral	$C_{10}H_{16}O$	27°	0·886	1429	55·3
10	Thymene oil	$C_{10}H_{16}$ (?)	28°	0·855	1322	66·9
11	Oil of turpentine	..	27°	0·893	1280	68·4

TABLE II.

Comparison of velocities.

Liquid	International Critical Table		Author	
	Temp. in°C.	Velocity	Temp. in°C.	Velocity
o-Nitro-toluene	20°·5	1482 m./s.	28°·0	1451 m./s.

3. *Discussion.*

We discuss below the relationship between the chemical constitution and sound velocity in the compounds experimented upon in this paper.

Esters.

Ethyl carbonate: This is a compound derived from the hypothetical carbonic acid with (OC_2H_5) replacing the two (OH) groups. In Part II it was shown that the di-esters, *i.e.*, esters of dibasic acids with two —COOH groups, usually have higher velocity, whereas results in Part I indicate that

the acoustic velocities are much lower for mono-esters. The velocity for this compound is much nearer to the velocity in the latter class of compounds, which is indicative of many of its properties.

Ethyl caprylate: This is an ester of a long-chain acid and the velocity corresponds to a compound of the aliphatic class.

Methyl salicylate: Methyl salicylate contains a benzene ring and we find that the velocity has reached 1408 m./s. at 28° C. This is characteristic of the aromatic compounds, for which the velocity is usually high.

Geranyl acetate: This is a long chain aliphatic compound, but we find that the velocity is 1328 m./s. at 28° C., which is rather high for a compound of the aliphatic class. The viscosity of this compound is high and it seems possible that the enhanced velocity is connected with this fact.

Nitro-Compounds.

Nitrotoluenes: (ortho and meta): The velocities in these two compounds are almost the same, their densities also remaining practically identical. The velocity is 1451 m./s. at 28° C.

Nitrobenzene and nitrotoluenes: The acoustic velocity in nitrobenzene is only slightly higher than that for the nitrotoluenes, the difference being only 4 metres. They are very nearly the same for these three compounds.

Aldehydes.

Salicylaldehyde: Here again the aromatic nature of the compound is indicated by the high velocity of 1474 m./s. at 27° C. This is higher than that for benzene or toluene.

Citral: The high velocity of 1429 m./s. at 27° C. for this aliphatic compound indicates that mere length of the molecule alone does matter. As pointed out in the case of geranyl acetate, a rather high viscosity for this compound must have enhanced the velocity. The density for this compound is comparable to any of the mono-esters, but the compressibility is low.

A full discussion on the relation between acoustic velocity and chemical constitution, for all compounds, for which acoustic velocities have been determined by the author, will be published shortly elsewhere.

The author thanks Sir C. V. Raman, KT., F.R.S., N.L., for his unfailing interest in the work.

4. Summary.

The paper gives determinations of acoustic velocity, by the method of diffraction of light by high frequency sound waves, in four esters, three nitro-compounds, two aldehydes, in thymene oil and in oil of turpentine. Adiabatic compressibilities have also been given.

DECOMPOSITIONS INTO CUBES OF PRIMES (II).

By Hansraj Gupta.

(From the Department of Mathematics, Govt. College, Hoshiarpur.)

Received May 25, 1936.

(Communicated by Mr. N. S. Nagendra Nath.)

1. Elsewhere* I have stated—

Conjecture A. All positive integral numbers can be expressed as the sums of at the most 13 cubes of primes $\geqslant 1$; and

Conjecture B. 1301 is the only number which cannot be expressed as the sum of less than 13 cubes of primes.

I now put forth

Conjecture C. All positive integral numbers $i \geqslant 8162$, can be expressed as the sums of at the most 11 cubes of primes $\geqslant 1$.

2. With the help of the two tables given at the end of this paper, I have been able to express almost every $i \leqslant 20875$, as the sum of at the most 11 cubes of primes. The following "idosyncratic numbers" are the only ones which seem to require as many as 12 cubes :

958 ; 1176 ; 1255 ; 1266 ; 1274 ; 1293 ; 1300 ; 1326 ; 1919 ; 1946 ; 2164 ; 3991 ; 4108 ; 4206 ; 4857 ; 6187 ; 6517 ; 8161 ; while 1301 requires 13 cubes as stated before.

Table I gives the minimum weight of all numbers $N \leqslant 1330$, in terms of cubes of primes. Table II lists some numbers whose weight is $\leqslant 6$, in general.

The work of verification mainly consists in breaking a number i into two parts N and M, such that the sum of the weights of N and M does not exceed 11. We take N from Table I and M from Table II.

3. It is now easy to show that

All positive integers $i \leqslant 10^5$, $i \neq 1301$, can be expressed as sums of at the most 12 cubes of primes.

This adds to the strength of conjectures A and B.

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* *Jour. London Math. Soc.*, 1935, **10**.

TABLE I.

N	0	1	2	3	4	5	6	7	8	9
		1	2	3	4	5	6	7	1	2
1	3	4	5	6	7	8	2	3	4	5
2	6	7	8	9	3	4	5	1	2	3
3	4	5	4	5	6	2	3	4	5	6
4	5	6	7	3	4	5	6	7	6	7
5	8	4	5	6	2	3	4	5	6	5
6	6	7	3	4	5	6	7	6	7	8
7	4	5	6	7	8	7	8	9	5	6
8	7	3	4	5	6	7	6	7	8	4
9	5	6	7	8	7	8	9	5	6	7
10	8	9	8	9	10	6	7	8	4	5
11	6	7	8	7	8	9	5	6	7	8
12	9	8	9	10	6	1	2	3	4	5
13	6	7	7	2	3	4	5	6	7	8
14	8	3	4	5	6	7	8	9	9	4
15	5	6	2	3	4	5	6	5	6	7
16	3	4	5	6	7	6	7	8	4	5
17	6	7	8	7	8	9	5	6	7	3
18	4	5	6	7	6	7	8	4	5	6
19	7	8	7	8	9	5	6	7	8	9
20	8	9	10	6	7	8	4	5	6	7
21	8	7	8	9	5	6	7	8	9	8
22	9	10	6	7	8	9	10	9	10	11
23	7	8	9	5	6	7	8	9	8	9
24	10	6	7	8	9	10	9	10	11	7
25	2	3	4	5	6	7	8	8	3	4
26	5	6	7	8	9	9	4	5	6	7
27	8	9	10	10	5	6	7	3	4	5
28	6	7	6	7	8	4	5	6	7	8
29	7	8	9	5	6	7	8	9	8	9
30	10	6	7	8	4	5	6	7	8	7
31	8	9	5	6	7	8	9	8	9	10
32	6	7	8	9	10	9	10	11	7	8
33	9	5	6	7	8	9	8	9	10	6
34	7	8	9	1	2	3	4	5	6	7
35	8	2	3	4	5	6	7	8	6	3
36	4	5	6	7	8	9	7	4	5	6
37	2	3	4	5	6	3	4	5	3	4
38	5	6	7	4	5	6	4	5	6	7
39	8	5	6	7	5	6	7	3	4	5

N	0	1	2	3	4	5	6	7	8	9
40	6	7	4	5	6	4	5	6	7	8
41	5	6	7	5	6	7	8	9	6	7
42	8	6	7	8	4	5	6	7	8	5
43	6	7	5	6	7	8	9	6	7	8
44	6	7	8	9	10	7	8	9	7	8
45	9	5	6	7	8	9	6	7	8	6
46	7	8	9	10	7	8	9	7	2	3
47	4	5	6	7	8	8	3	4	5	6
48	7	8	9	7	4	5	6	7	8	9
49	10	8	5	6	7	3	4	5	6	7
50	4	5	6	4	5	6	7	8	5	6
51	7	5	6	7	8	9	6	7	8	6
52	7	8	4	5	6	7	8	5	6	7
53	5	6	7	8	9	6	7	8	6	7
54	8	9	10	7	8	9	7	8	9	5
55	6	7	8	9	6	7	8	6	7	8
56	9	10	7	8	9	7	8	9	10	11
57	8	9	10	8	9	10	6	7	8	9
58	10	7	8	9	7	8	9	10	11	8
59	9	10	8	3	4	5	6	7	8	9
60	9	4	5	6	7	8	9	10	8	5
61	6	7	8	9	10	11	9	6	7	8
62	4	5	6	7	8	5	6	7	5	6
63	7	8	9	6	7	8	6	7	8	9
64	10	7	8	9	7	8	9	5	6	7
65	8	9	6	7	8	6	7	8	9	10
66	7	8	9	7	8	9	10	11	8	9
67	10	8	9	10	6	7	8	9	10	7
68	8	9	7	8	9	10	2	3	4	5
69	6	7	8	9	3	4	5	6	7	8
70	9	7	4	5	6	7	8	9	10	8
71	5	6	7	3	4	5	6	7	4	5
72	6	4	5	6	7	8	5	6	7	5
73	6	7	8	9	6	7	8	6	7	8
74	4	5	6	7	8	5	6	7	5	6
75	6	7	8	6	7	8	6	7	7	8
76	9	7	8	9	7	8	8	5	6	7
77	8	9	6	7	8	6	7	7	8	9
78	7	8	9	7	8	8	9	10	8	9
79	10	8	9	9	6	7	8	9	10	7

N	0	1	2	3	4	5	6	7	8	9
80	8	9	7	8	8	9	10	8	9	10
81	8	3	4	5	6	7	8	9	9	4
82	5	6	7	8	9	10	8	5	6	7
83	8	9	10	11	9	6	7	8	4	5
84	6	7	8	5	6	7	5	6	7	8
85	9	6	7	8	6	7	8	9	10	7
86	8	9	7	8	9	5	6	7	8	9
87	6	7	8	6	7	7	8	9	7	8
88	9	7	8	8	9	10	8	9	10	8
89	9	9	6	7	8	9	10	7	8	9
90	7	8	8	9	10	8	9	10	8	9
91	9	10	11	9	10	11	9	10	10	7
92	8	9	10	11	8	9	10	8	9	9
93	10	11	9	10	11	9	4	5	6	7
94	8	9	10	10	5	6	7	8	9	10
95	11	9	6	7	8	9	10	11	12	10
96	7	8	9	5	6	7	8	9	6	7
97	8	6	7	8	9	10	7	8	9	7
98	8	9	10	11	8	9	10	8	9	10
99	6	7	8	9	10	7	8	9	7	8
100	8	9	10	8	9	10	8	9	9	10
101	11	9	10	11	9	10	10	7	8	9
102	10	11	8	9	10	8	9	9	10	3
103	4	5	6	7	8	9	10	4	5	6
104	7	8	9	10	8	5	6	7	8	9
105	10	11	9	6	7	8	4	5	6	7
106	8	5	6	7	5	6	7	8	9	6
107	7	8	6	7	8	9	10	7	8	9
108	7	8	9	5	6	7	8	9	6	7
109	8	6	7	7	8	9	7	8	9	7
110	8	8	9	10	8	9	10	8	9	9
111	6	7	8	9	10	7	8	9	7	8
112	8	9	10	8	9	9	8	9	9	10
113	11	9	10	10	9	10	10	7	8	9
114	10	11	8	9	10	8	9	9	10	11
115	9	10	10	9	4	5	6	7	8	9
116	10	10	5	6	7	8	9	10	11	9
117	6	7	8	9	10	11	12	10	7	8
118	9	5	6	7	8	9	6	7	8	6
119	7	8	9	10	7	8	9	7	8	9

N	0	1	2	3	4	5	6	7	8	9
120	10	11	8	9	10	8	9	10	6	7
121	8	9	10	7	8	9	7	8	8	9
122	10	8	9	10	8	9	9	10	11	9
123	10	11	9	10	10	7	8	9	10	11
124	8	9	10	8	9	9	10	11	9	10
125	10	9	10	10	11	12	10	11	11	10
126	11	11	8	9	10	11	12	9	10	11
127	9	10	10	11	12	10	11	11	10	5
128	6	7	8	9	10	11	11	6	7	8
129	9	10	11	12	10	7	8	9	10	11
130	12	13	11	8	9	10	6	7	8	9
131	10	7	8	9	7	8	9	10	11	8
132	9	10	8	9	10	11	12	9	10	11
133	9									

TABLE II.

M	wt.	M	wt.	M	wt.	M	wt.	M	wt.
1331	1	8387	5	12167	1	16160	4	18411	3
1372	4	8441	3	12488	4	16166	4	18455	5
2197	1	8784	4	12584	4	16380	4	18577	5
2360	4	8788	4	13103	3	16413	5	18631	3
2662	2	8906	4	13300	6	16417	5	18754	4
2703	5	9056	2	13354	4	16503	5	18758	4
3005	3	9131	5	13450	4	16509	5	18882	4
3348	4	9249	5	13498	2	16561	3	19026	2
3528	2	9253	5	13718	2	16685	3	19101	5
3569	5	9307	3	13841	3	16904	4	19223	5
3871	3	9470	6	14364	2	16936	4	19277	3
3983	3	9521	3	14527	5	16974	6	19598	6
4214	4	9772	4	14739	3	17026	4	19620	4
4336	4	9826	2	14781	5	17080	2	19652	4
4394	2	9864	4	14829	3	17246	4	19712	4
4859	3	10237	5	15049	3	17369	5	19742	4
4900	6	10387	3	15082	4	17401	5	19908	6
4913	1	10584	6	15172	4	17491	5	19945	7
5080	4	10638	4	15246	6	17497	5	19962	4
5667	5	10730	4	15300	4	17589	5	20085	5
5725	3	10852	4	15392	4	17766	4	20089	5
6068	4	10981	5	15515	5	17844	6	20213	5
6190	4	10985	5	15551	5	17892	4	20305	5
6244	2	11157	3	15643	5	18016	4	20309	5
6591	3	11253	3	15647	5	18112	4	20357	3
7110	2	11500	4	15695	3	18235	5	20560	6
7575	3	11504	4	15735	5	18267	5	20577	3
7922	4	11718	4	15915	3	18357	5	20608	4
7986	6	11772	2	16038	4	18359	5	20700	4
8190	2	12023	3	16070	4	18363	5	20828	4

THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: GENERALISED THEORY.

The Asymmetry of the Diffraction Phenomena at Oblique Incidence.

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1. Introduction.

In a series of five papers[1] published in these *Proceedings*, the theory of the diffraction of light by high frequency sound waves has been developed. There have been however two stages in the development of the theory. The first one had a restriction in the theory in order to simplify the treatment of the problem and bring out its essential features without unnecessary complications. In the second one, the above restriction in the theory has been removed and the theory of the phenomenon under general conditions has been developed. The general theory includes the preliminary one as a special case.

Preliminary Theory.—In Parts I, II and III, the essential idea is that the optical effects are due to the corrugated form of the emerging wave-front and that the corrugations due to the density fluctuations could be simply calculated by the phase changes accompanying the traversing beam ignoring the amplitude changes. The exact condition under which this restriction could be realised in practice is indicated in the papers. The theory accounts for the appearance of a large number of diffraction orders and also the wandering of the intensity of light amongst them as the length of the cell, the supersonic intensity and the wave-length of the incident light are changed. All these results have been strikingly confirmed quantitatively by Bär[2] who actually realised in practice the restriction we had imposed in our preliminary theory. The intensity variations and the symmetry of the diffraction effects in the case of oblique incidence have been also confirmed by Bär.[2] In Part III of the theory, we investigated the Doppler effects in the diffraction orders when the supersonic wave is either a progressive one or a standing

[1] C. V. Raman and N. S. Nagendra Nath, *Proc. Ind. Acad. Sci.*, 1935, **2**, 406 and 413; 1936, **3**, 75, 119 and 459.

[2] R. Bär, *Helv. Phy. Acta.*, 1936. Bär realised it by diminishing the frequency of the supersonic waves.

one. The results in the case of a standing wave are really interesting. We obtained the result that any order would cohere partly with any other order counted in an even sequence from it while it would not cohere with the remaining ones lying on an odd sequence from it. This result is in remarkable agreement with the same result obtained by Bär[3] experimentally.

Generalised Theory.—In Parts IV and V, the restriction of the preliminary theory was removed by considering the partial differential equation governing the propagation of light in a quasi-homogeneous medium. The results regarding the coherence phenomena amongst the diffraction orders were found to be true even if the supersonic wave be a general periodic progressive one or a standing one. We then considered the cases of a simple periodic progressive wave and a standing wave to investigate the amplitudes of the various diffraction orders. A difference—differential equation was obtained whose solutions correspond to the amplitudes of the diffraction orders. This equation enabled us to show that, in the case of oblique incidence, the diffraction pattern will be, in general, asymmetric which agrees with the results of Debye and Sears, Lucas and Biquard, Bär and Parthasarathy. The purpose of this paper is to solve the difference—differential equation occurring in the theory by the series method and offer an explanation for the quantitative experimental results obtained by Parthasarathy[5] in the case of the oblique incidence.

In this connection we desire to make some remarks regarding Brillouin's theory. The idea of characteristic reflection in these experiments does not seem very appropriate in view of the fact that the wave-length of the periodic fluctuation of the density is large compared with the wave-length of the light. The concept of reflection does not explain the presence of other orders and the *non-sharpness* of the maximum intensity of the reflected order at the characteristic obliquity of light to the sound waves. Thus, the use of the general word '*propagation*' is certainly preferable to the word '*reflection*' *for we know only and are here concerned with the equation governing the propagation of light in the medium.* In Brillouin's rigorous theory[4] of the diffraction phenomenon, he starts from the well-known partial differential equation governing the propagation of light in a quasi-homogeneous medium as we have also done. Thus the basis of Brillouin's rigorous theory and our general theory are the same. But the developments of the theory are different. His fundamental idea is that the emerging wave-front will be equivalent

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[3] R. Bär, *Helv. Phy. Acta.*, 1935, **8**, 591.

[4] L. Brillouin, *Act. Sci. et Ind.*, 1933, **59**.

[5] S. Parthasarathy, *Proc. Ind. Acad. Sci.*, 1936, **3**, 594.

to a set of plane waves travelling in the same direction of the incident light but with an amplitude grating on each one of them given by a multiple of a Mathieu Function. This analysis though perfect leads to complicated difficulties for, to find the diffraction effects in any particular direction, one will have to find the effects due to all the analysed waves. On the other hand, we have analysed the emerging corrugated wave into a set of plane waves inclined to one another at the characteristic diffracted angles. To find the diffraction effects in any particular direction, one has only to consider the plane wave travelling in that direction. Our analysis led in the preliminary theory to results which have been later beautifully confirmed by Bär[2] and, in the general theory, has answered satisfactorily the occurrence of the coherence phenomena and the asymmetry in the intensity of the diffraction orders in the case of oblique incidence.

2. Propagation of Light in a Quasi-Homogeneous Medium.

In Parts IV and V, the wave-function governing the propagation of light in a medium was assumed to satisfy the partial differential equation

$$\nabla^2 \psi = \left[\frac{\mu(x, y, z, t)}{c}\right]^2 \frac{\partial^2 \psi}{\partial t^2}$$

or

$$\nabla^2 \psi = \frac{k}{c^2} \frac{\partial^2 \psi}{\partial t^2} \qquad \ldots \quad (1)$$

when the frequency of the time variation of $\mu\,(x, y, z, t)$ is very slow compared to that of the wave-function of light. This would be so in the case of a medium filled with sound waves, for the frequency of the time variation of $\mu\,(x, y, z, t)$ corresponds to the frequency of the sound waves which is negligible compared to the frequency of the sound waves.

We desire to point out that the equation (1) can be derived on the basis of the electromagnetic equations if we assume that the medium is non-magnetic and transparent and that ν^*, the frequency of sound waves, is small compared to ν, the frequency of the incident light.

The Maxwell equations† for the propagation of electromagnetic waves in the medium are

$$\text{rot}\,\vec{E} = -\frac{1}{c}\frac{\partial \vec{H}}{\partial t}, \qquad \text{div}\,\vec{H} = 0,$$

$$\text{rot}\,\vec{H} = \frac{1}{c}\frac{\partial \vec{D}}{\partial t}, \qquad \text{div}\,\vec{D} = 0, \qquad \ldots \quad (2)$$

where

$$\vec{D} = k\,\vec{E}$$

† Frenkel's *Elektrodynamik*, 1928, page 236.

k being the dielectric constant of the medium as a function of x, y, z, and t. Eliminating $\vec{H}$, one obtains

$$\frac{1}{c^2}\frac{\partial^2 \vec{D}}{\partial t^2} = \nabla^2 \vec{E} + \frac{\nabla k}{k} \text{ rot } \vec{E} + \left(\frac{\nabla k}{k} \nabla\right) \vec{E} + (\vec{E} \nabla) \frac{\nabla k}{k} \ldots \quad (3)$$

Since $\nu^* << \nu$

$$| \nabla k | \lambda << 1.$$

This reduces (3) to

$$\frac{1}{c^2}\frac{\partial^2 \vec{D}}{\partial t^2} = \nabla^2 \vec{E}$$

or

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}(k \vec{E}) = \nabla^2 \vec{E} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

Using again the assumption that the frequency of the time variation of k is small compared to that of $\vec{E}$, the equation (4) reduces to

$$\frac{k}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} = \nabla^2 \vec{E} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

One can find some discussions of this equation in *Frenkel's "Electrodynamik," (Zweiter Band)*.

3. Generalised Theory of the Phenomenon.

The equation governing the propagation of light in the medium we are considering is

$$\nabla^2 \psi = \left[\frac{\mu (X, Y, Z, t)}{c}\right]^2 \frac{\partial^2 \psi}{\partial t^2} \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

We choose the axes of reference such that the Z-axis points to the direction of the propagation of the incident light and the X-axis is contained in a plane perpendicular to the sound waves containing the direction of the propagation of the incident light. This choice of the axes of reference enables us to ignore the dependence of ψ on Y and write the differential equation as

$$\frac{\partial^2 \psi}{\partial X^2} + \frac{\partial^2 \psi}{\partial Z^2} = \left[\frac{\mu (X, Z, t)}{c}\right]^2 \frac{\partial^2 \psi}{\partial t^2} \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

If $\mu (X, Z, t)$ did not depend on time, ψ would have had the only time factor $\exp [2\pi i \nu t]$. Considering the actual case where $\mu (X, Z, t)$ depends on time, we can write ψ as given by

$$\psi = \exp [2\pi i \nu t] \Phi (X, Z, t) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (8)$$

where Φ varies slowly in time compared to $\exp [2\pi i \nu t]$ for $\nu^* << \nu$. It can be seen easily that

$$\left| 4\pi\nu \frac{\partial \Phi}{\partial t} \right| << | 4\pi^2\nu^2\Phi | \text{ and } \left| \frac{\partial^2 \Phi}{\partial t^2} \right| << | 4\pi^2\nu^2\Phi |.$$

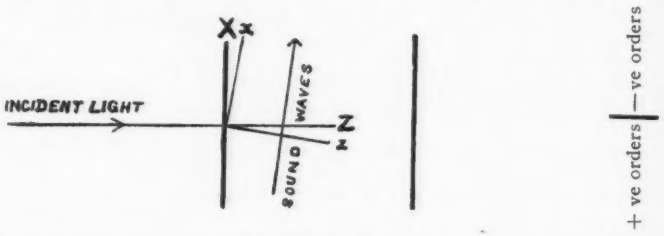
Thus we can reduce the differential equation to

$$\frac{\partial^2 \Phi}{\partial X^2} + \frac{\partial^2 \Phi}{\partial Z^2} = -\frac{4\pi^2}{\lambda^2} [\mu (X, Z, t)]^2 \Phi \quad .. \quad .. \quad .. \quad (9)$$

and obtain ψ by the equation

$$\psi = \exp [2\pi i \nu t] \ \Phi.$$

The following figure gives the schematic representation of the phenomenon we are considering. The angle between the sound wave-fronts and



the direction of propagation of the incident light is ϕ. The x-axis points to the direction of propagation of the sound waves and the z-axis is contained in the plane containing the X-axis and the Z-axis. Thus $\cos\phi$ and $\sin\phi$ are the z- and the x- direction cosines of the direction of propagation of the incident light.

Even if we consider a general periodic sound disturbance with the period λ^* along the x-axis, the symmetry of the experiment with respect to the wave-fronts demands

$$\Phi (X, Z, t) = \Phi (X + p\lambda^* \sec\phi, Z, t) \quad .. \quad .. \quad .. \quad (10)$$

where p is an integer. This is true for, if we imagine a translation of the sound waves by a distance $p\lambda^* \sec\phi$ along the X-axis, the experimental conditions are the same as before. As the sound wave-fronts repeat themselves with the ferquency ν^*, Φ should be periodic in time with frequency ν^*, *i.e.*,

$$\Phi (X, Z, t) = \Phi \left(X, Z, t + \frac{q}{\nu^*}\right) \quad .. \quad .. \quad .. \quad (11)$$

where q is an integer. The conditions (10) and (11) enable us to write down the double Fourier expansion of Φ as given by

$$\sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{rs} (Z) \, e^{2\pi i r X \cos\phi/\lambda^*} \, e^{2\pi i s \nu^* t} \quad .. \quad .. \quad .. \quad (12)$$

Progressive Sound Waves.—In the case of progressive sound waves travelling along the positive direction of the x-axis, we have the property that

$$\Phi (X + \rho\lambda^* \sec\phi, Z, t) = \Phi (X, Z, t - \rho/\nu^*) \quad .. \quad .. \quad (13)$$

where ρ is any number. This condition enables us to write (12) as

$$\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{rs}(\mathrm{Z})\, e^{2\pi i r \mathrm{X}\cos\phi/\lambda^*}\, e^{2\pi i s\nu^* t}\, e^{2\pi i r\rho}$$

$$= \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{rs}(\mathrm{Z})\, e^{2\pi i r \mathrm{X}\cos\phi/\lambda^*}\, e^{2\pi i s\nu^* t}\, e^{-2\pi i s\rho} \quad .. \quad .. \quad (14)$$

Comparing the Fourier coefficients on each side of (14), we get

$$f_{rs}(\mathrm{Z})\, e^{2\pi i r\rho} = f_{rs}(\mathrm{Z})\, e^{-2\pi i s\rho} \quad .. \quad .. \quad .. \quad .. \quad (15)$$

where ρ is any number. This could only be true if

$$f_{rs}(\mathrm{Z}) = 0 \qquad \text{when } r \neq -s \quad .. \quad .. \quad .. \quad .. \quad (16)$$

The condition (16) restricts the number of terms in the Fourier expansion of Φ so that it can be written as given by

$$\Phi = \sum_{-\infty}^{\infty} f_r(\mathrm{Z})\, e^{2\pi i r \mathrm{X}\cos\phi/\lambda^*}\, e^{-2\pi i r\nu^* t} \quad .. \quad .. \quad .. \quad (17)$$

so that ψ is given by

$$\psi = \Sigma f_r(\mathrm{Z})\, e^{2\pi i r \mathrm{X}\cos\phi/\lambda^*}\, e^{2\pi i(\nu - r\nu^*)t} \quad .. \quad .. \quad .. \quad (18)$$

If one considers the diffraction effects of ψ given by (18) it will be fairly obvious that the rth order diffraction component will be inclined at an angle $\sin^{-1}(-r\lambda\cos\phi/\lambda^*)$ with the incident beam of light, will have the frequency $\nu - r\nu^*$ and the relative intensity $|f_r(\mathrm{Z})|^2$

Standing Sound Waves.—In this case

$$\Phi\left(\mathrm{X} + \frac{p\lambda^* \sec\phi}{2}, \mathrm{Z}, t\right) = \Phi\left(\mathrm{X}, \mathrm{Z}, t \pm \frac{p}{2\nu^*}\right) \quad .. \quad .. \quad (19)$$

where p is an integer. Using (19) in (12) we get

$$\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{rs}(\mathrm{Z})\, e^{2\pi i r \mathrm{X}\cos\phi/\lambda^*}\, e^{2\pi i s\nu^* t}\, e^{\pi i r p}$$

$$= \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{rs}(\mathrm{Z})\, e^{2\pi i r \mathrm{X}\cos\phi/\lambda^*}\, e^{2\pi i s\nu^* t}\, e^{\pm \pi i s p} \quad .. \quad .. \quad (20)$$

Comparing the Fourier coefficients in the above, we get

$$f_{rs}(\mathrm{Z})\, e^{\pi i r p} = f_{rs}(\mathrm{Z})\, e^{\pm \pi i s p} \quad .. \quad .. \quad .. \quad .. \quad (21)$$

where p is an integer. (21) could only be true if all $f_{rs}(\mathrm{Z})$ are zero except those in which r and s are both odd or both even. So the Fourier expansion for Φ in this case is

$$\Phi = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{2r,2s}(\mathrm{Z})\, e^{2\pi i 2r \mathrm{X}\cos\phi/\lambda^*}\, e^{2\pi i 2s\nu^* t}$$

$$+ \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{2r+1,2s+1}(\mathrm{Z})\, e^{2\pi i \overline{2r+1} \mathrm{X}\cos\phi/\lambda^*}\, e^{2\pi i \overline{2s+1}\nu^* t} \quad .. \quad (22)$$

Thus

$$\psi = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{2r,2s}(\mathrm{Z})\, e^{2\pi i 2r\mathrm{X}\cos\phi/\lambda^*}\, e^{2\pi i(\nu+2s\nu^*)t} + \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{2r+1,2s+1}(\mathrm{Z})\, e^{2\pi i\overline{2r+1}\mathrm{X}\cos\phi/\lambda^*}\, e^{2\pi i(\nu+\overline{2s+1}\nu^*)t} \quad .. \quad (23)$$

If one considers the diffraction effects of ψ given by (23), it is fairly obvious that the diffraction orders could be divided into two groups, one containing the even ones and the other odd ones; any even order would contain radiations with frequencies ν, $\nu \pm 2\nu^*$,— —, $\nu \pm 2r\nu^*$,— — and any odd order would contain radiations with frequencies $\nu \pm \nu^*$, $\nu \pm 3\nu^*$, — —, $\nu \pm \overline{2r+1}\,\nu^*$, — —. It should be remembered that the above results are valid for sound waves which are *general periodic* and either progressive as in the preceding case or standing as in the present case.

General Periodic Sound Waves.—In the case of sound waves which are neither progressive nor standing we should expect, from (12), any order to contain radiations with frequencies $\nu + r\nu^*$ where r is an integer both positive and negative. So, any two orders, *in general*, cohere partly for they contain radiations with the same wave-lengths. It is worthwhile to show that this is true by an experiment, taking care that the wave is neither progressive nor standing.

4. The Case when the Disturbance in the Medium is Progressive and Simple Harmonic.

If we suppose that the variation in the refractive index of the medium is simple harmonic and progressive along the x-axis, it can be represented as

$$\mu(x,t) - \mu_0 = \mu \sin 2\pi(\nu^* t - x/\lambda^*) \quad .. \quad .. \quad .. \quad (24)$$

where μ_0 is the constant refractive index of the medium when the sound waves are not present and μ is the amplitude of the variation of the refractive index when the sound waves are present. It can be written as

$$-\frac{\mu}{2i}\left\{e^{i(bx-\epsilon)} - e^{-i(bx-\epsilon)}\right\}$$

or

$$-\frac{\mu}{2i}\left\{e^{i(b\mathrm{X}\cos\phi + \mathrm{Z}\sin\phi - \epsilon)} - e^{-i(b\mathrm{X}\cos\phi + \mathrm{Z}\sin\phi - \epsilon)}\right\} \quad .. \quad (25)$$

where $\epsilon = 2\pi\nu^* t$ and $b = 2\pi/\lambda^*$.

We know that Φ satisfies the equation

$$\frac{\partial^2\Phi}{\partial \mathrm{X}^2} + \frac{\partial^2\Phi}{\partial \mathrm{Z}^2} = -\frac{4\pi^2}{\lambda^2}\{\mu(\mathrm{X},\mathrm{Z},t)\}^2\Phi \quad .. \quad .. \quad .. \quad (26)$$

with the representation for it as

$$\sum_{-\infty}^{\infty} f_r(Z)\, e^{2\pi i r X \cos\phi/\lambda^*}\, e^{-2\pi i r \nu^* t} \quad .. \quad .. \quad .. \quad (27)$$

Substituting the Fourier series (27) and the expression (25) for μ (X, Z, t) in the equation (26) and neglecting the second order term with the coefficient μ^2, we get by comparing the coefficients

$$\frac{d^2 f_r}{d Z^2} - \frac{4\pi^2 r^2 \cos^2\phi}{\lambda^{*2}} f_r - A f_r = \frac{B}{2i}\left\{ f_{r-1}\, e^{ibZ\sin\phi} - f_{r+1}\, e^{-ibZ\sin\phi} \right\} \quad .. \quad .. \quad .. \quad (28)$$

where $A = -4\pi^2\mu_0^2/\lambda^2$ and $B = 8\pi^2\mu_0\mu/\lambda^2$. Putting $f_r(Z) = \exp(-iu\mu_0 Z)\, \Phi_r(Z)$ where $u = 2\pi/\lambda$ and putting $Z = (2\pi\mu)^{-1}\lambda\xi$, we obtain

$$\mu^2 \frac{d^2\Phi_r}{d\xi^2} - 2i\mu_0\mu \frac{d\Phi_r}{d\xi} - \frac{r^2\lambda^2\cos^2\phi}{\lambda^{*2}}\Phi_r = -\mu_0\mu i\left\{\Phi_{r-1}\, e^{ia\xi\sin\phi} - \Phi_{r+1}\, e^{-ia\xi\sin\phi}\right\} \quad .. \quad .. \quad (29)$$

where $a = \lambda/\mu\lambda^*$.

As μ is very small compared to μ_0, we may consider the equation

$$2\frac{d\Phi_r}{d\xi} - (\Phi_{r-1}\, e^{ia\xi\sin\phi} - \Phi_{r+1}\, e^{-ia\xi\sin\phi}) = \frac{ir^2\lambda^2\cos^2\phi}{\mu_0\mu\lambda^{*2}}\Phi_r \quad .. \quad (30)$$

Denoting $\frac{\lambda^2\cos^2\phi}{\mu_0\mu\,\lambda^{*2}}$ by ρ and putting $\Phi_r = \Psi_r\, e^{ira\xi\sin\phi}$ .. (31)

we get

$$2\frac{d\Psi_r}{d\xi} - \Psi_{r-1} + \Psi_{r+1} = i\,(r^2\rho - 2ra\sin\phi)\,\Psi_r \quad .. \quad (32)$$

The boundary conditions of the problem are

$$\Psi_r(0) = 0, \quad r \neq 0$$

and $$\Psi_0(0) = 1. \quad .. \quad .. \quad .. \quad .. \quad (33)$$

The solution of the equation for Ψ's seems to be not quite easy in terms of the well-known functions. We have therefore attempted here to solve the equation, a little more generalised, by the series method.

5. *Solution of the Difference—Differential Equation by the Series Method.*

Consider the following equation†

$$2\frac{d\Psi_r}{dx} - \Psi_{r-1} + \Psi_{r+1} = c_r\Psi_r \quad .. \quad .. \quad .. \quad (34)$$

† Throughout this section, x is used for ξ of the previous section for convenience.

where r is an integer ranging from $-\infty$ to ∞ and c_r is a constant depending only on r. The boundary conditions of the problem are

$$\Psi_r(0) = 0,\ r \neq 0 \quad \text{and} \quad \Psi_0(0) = 1 \qquad \ldots\ (35)$$

Let us write the series representations for Ψ's as given by

$$\Psi_n = \frac{x^n}{2^n n!} \sum_{r=0}^{\infty} A_{n,r}\, x^r \qquad \text{for } n \geqslant 0 \qquad \ldots\ (36)$$

and

$$\Psi_n = \frac{x^{|n|}}{2^{|n|}|n|!} \sum_{r=0}^{\infty} A_{n,r}\, x^r \qquad \text{for } n < 0 \qquad \ldots\ (37)$$

These representations satisfy the boundary conditions (35) if

$$A_{0,0} = 1 \qquad \ldots\ (38)$$

Case I. Let $n \geqslant 1$. Then

$$\Psi_n = \frac{x^n}{2^n n!} \sum_{0}^{\infty} A_{n,r}\, x^r$$

$$\frac{d\Psi_n}{dx} = \frac{1}{2^n n!} \sum_{0}^{\infty} (n + r)\, A_{n,r}\, x^{(n+r-1)}$$

$$\Psi_{n-1} = \frac{1}{2^{n-1} n-1!} \sum_{0}^{\infty} A_{n-1,r}\, x^{n+r-1} \qquad \ldots\ (39)$$

and $$\Psi_{n+1} = \frac{1}{2^{n+1}(n+1)!} \sum_{0}^{\infty} A_{n+1,r}\, x^{n+r+1}.$$

Substituting (39) in (34) and comparing the coefficients on both sides of the equation, we get the difference equation

$$(n + r + 1)\, A_{n,r+1} - n\, A_{n-1,r+1} + \frac{1}{4(n+1)} A_{n+1,r-1} = \frac{c_n}{2} A_{n,r} \qquad \ldots\ (40)$$

where n ranges from 1 to ∞ and r ranges from 0 to ∞.

Case II. Let $n = 0$. Then

$$\frac{d\Psi_0}{dx} = \sum_{0}^{\infty} r\, A_{0,r}\, x^{r-1}$$

$$\Psi_{-1} = \tfrac{1}{2} \sum_{0}^{\infty} A_{-1,r}\, x^{r+1} \qquad \ldots\ (41)$$

$$\Psi_1 = \tfrac{1}{2} \sum_{0}^{\infty} A_{1,r}\, x^{r+1}$$

Substituting (41) in (34) and comparing the coefficients, we get

$$2(r+1)\,A_{0,r+1} - \tfrac{1}{2}\,A_{-1,r-1} + \tfrac{1}{2}\,A_{1,r-1} = 0 \quad .. \quad .. \quad (42)$$

Case III.—Let $n \leqslant -1$. Then

$$\left.\begin{aligned} \Psi_n &= \frac{x^m}{2^m m!}\,\Sigma\,A_{n,r}\,x^r \text{ where } n = -m, \\ \frac{d\Psi_n}{dx} &= \frac{1}{2^m m!}\,\Sigma\,(m+r)\,A_{n,r}\,x^{m+r-1} \\ \Psi_{n-1} &= \frac{1}{2^{(m+1)}(m+1)!}\,\Sigma\,A_{n-1,r}\,x^{m+r+1} \\ \Psi_{n+1} &= \frac{1}{2^{(m-1)}(m-1)!}\,\Sigma\,A_{n+1,r}\,x^{m+r-1} \end{aligned}\right\} \quad .. \quad .. \quad (43)$$

Substituting (43) in (34), and comparing the coefficients, we get

$$(-n+r+1)\,A_{n,r+1} + \frac{1}{4(n-1)}\,A_{n-1,r-1} - n\,A_{n+1,r+1} = \frac{c_n}{2}A_{n,r} \quad (44)$$

Thus we have the following three difference equations to determine the coefficients of the terms in the power series (36) and (37).

$$\left.\begin{aligned} &n \geqslant 1,\ (n+r+1)\,A_{n,r+1} - n\,A_{n-1,r+1} + \frac{1}{4(n+1)}\,A_{n+1,r-1} = \frac{c_n}{2}\,A_{n,r} \\ &n = 0,\ 2(r+1)\,A_{0,r+1} - \tfrac{1}{2}\,A_{-1,r-1} + \tfrac{1}{2}\,A_{1,r-1} = 0 \\ &n \leqslant -1,\ (-n+r+1)\,A_{n,r+1} - n\,A_{n+1,r+1} + \frac{1}{4(n-1)}\,A_{n-1,r-1} = \frac{c_n}{2}\,A_{n,r} \end{aligned}\right\} \quad .. \quad (45)$$

Considering the first equation it can be seen that if we write c_{-n} for c_n, $(n \geqslant 1)$ and write $(-)^n\,A_{-n,r}$ for $A_{n,r}$, $(n \geqslant 1)$, we get the third equation. So it is only necessary to solve the first two equations of (45).

(A) Suppose $r = -1$. Then

$$n\,A_{n,0} - n\,A_{n-1,0} = 0,\ n \geqslant 1$$
$$A_{0,0} = 1 \quad \text{(boundary condition)}$$

Thus

$$A_{n,0} = 1, \qquad n \geqslant 0$$

and

$$A_{n,0} = (-)^n, \qquad n \leqslant -1 \quad .. \quad .. \quad .. \quad (46)$$

(B) Suppose $r = 0$. Then

$$(n+1)\,A_{n,1} - n\,A_{n-1,1} = \frac{c_n}{2}\,A_{n,0}, \qquad n \geqslant 1,$$
$$2\,A_{0,1} = 0.$$

(i) Let $n = 1$. Then

$$2\,A_{1,1} - A_{0,1} = \frac{c_1}{2}\,A_{1,0} = \frac{c_1}{2},$$
$$\therefore \quad A_{1,1} = c_1/4.$$

(ii) Let $n = 2$. Then

$$3\,A_{2,1} - 2\,A_{1,1} = \frac{c_2}{2}\,A_{2,0} = \frac{c_2}{2},$$

$$3\,A_{2,1} = \frac{c_2}{2} + 2\,A_{1,1}$$

$$= \frac{c_1 + c_2}{2}.$$

$$\therefore \quad A_{2,1} = \frac{c_1 + c_2}{6}.$$

(iii) Let $n = 3$. Then

$$4\,A_{3,1} - 3\,A_{2,1} = \frac{c_3}{2}.$$

$$\therefore \quad A_{3,1} = \frac{c_1 + c_2 + c_3}{8}.$$

(iv) Substituting $n = 4, 5$, we get $A_{4,1}$ and $A_{5,1}$.

Thus

$$A_{0,1} = 0$$

$$\left.\begin{aligned}
A_{1,1} &= \frac{c_1}{2\cdot 2}, & A_{-1,1} &= -\frac{c_{-1}}{2\cdot 2},\\
A_{2,1} &= \frac{c_1 + c_2}{2\cdot 3}, & A_{-2,1} &= \frac{c_{-1} + c_{-2}}{2\cdot 3},\\
A_{3,1} &= \frac{c_1 + c_2 + c_3}{2\cdot 4}, & A_{-3,1} &= -\frac{c_{-1} + c_{-2} + c_{-3}}{2\cdot 4},\\
A_{4,1} &= \frac{c_1 + c_2 + c_3 + c_4}{2\cdot 5}, & A_{-4,1} &= \frac{c_{-1} + c_{-2} + c_{-3} + c_{-4}}{2\cdot 5},\\
A_{5,1} &= \frac{c_1 + c_2 + c_3 + c_4 + c_5}{2\cdot 6}, & A_{-5,1} &= -\frac{c_{-1} + c_{-2} + c_{-3} + c_{-4} + c_{-5}}{2\cdot 6},
\end{aligned}\right\} \quad \ldots \quad (47)$$

(B) We will now calculate the coefficients $A_{n,2}$.

For this purpose we put $r = 1$ in (45) and obtain

$$(n + 2)\,A_{n,2} - n\,A_{n-1,2} + \frac{1}{4(n+1)}\,A_{n+1,0} = \frac{c_n}{2}\,A_{n,1} \quad \ldots \quad (48)$$

for $n \geqslant 1$ and

$$4\,A_{0,2} - \tfrac{1}{2}\,A_{-1,0} + \tfrac{1}{2}\,A_{1,0} = 0$$

(i) From (48) and using (46), we get

$$4\,A_{0,2} = -\tfrac{1}{2}\,A_{1,0} + \tfrac{1}{2}\,A_{-1,0} = -1$$

Thus $A_{0,2} = -\tfrac{1}{4}$.

(ii) Let $n = 1$. Then

$$3\,A_{1,2} - A_{0,2} + \frac{1}{4\cdot 2}A_{2,0} = \frac{c_1}{2}A_{1,1},$$

$$3\,A_{1,2} = -\frac{1}{4\cdot 2} - \tfrac{1}{4} + \frac{c_1^2}{2\cdot 2\cdot 2}$$

$$A_{1,2} = -\frac{1}{4\cdot 2} + \frac{c_1^2}{2\cdot 2\cdot 2\cdot 3}$$

(iii) Substituting $n = 2, 3, 4$ successively in (48), we get

$$A_{2,2} = -\frac{1}{4\cdot 3} + \frac{c_1^2 + c_1c_2 + c_2^2}{2\cdot 2\cdot 3\cdot 4}$$

$$A_{3,2} = -\frac{1}{4\cdot 4} + \frac{c_1^2+c_2^2+c_3^2 + c_1c_2+c_2c_3 + c_3c_1}{2\cdot 2\cdot 4\cdot 5}$$

$$A_{4,2} = -\frac{1}{4\cdot 5} + \frac{c_1^2 + c_2^2+c_3^2 + c_4^2 + c_1c_2 + c_2c_3 + c_3c_1 + c_1c_4 + c_2c_4 + c_3c_4}{2\cdot 2\cdot 5\cdot 6}$$

Thus

$$A_{-1,2} = \frac{1}{4\cdot 2} - \frac{c_{-1}^2}{2\cdot 2\cdot 2\cdot 3}$$

$$A_{-2,2} = -\frac{1}{4\cdot 3} + \frac{c_{-1}^2 + c_{-1}c_{-2} + c_{-2}^2}{2\cdot 2\cdot 3\cdot 4}$$

$$A_{-3,2} = \frac{1}{4\cdot 4} - \frac{c_{-1}^2 + c_{-2}^2 + c_{-3}^2 + c_{-1}c_{-2} + c_{-2}c_{-3} + c_{-3}c_{-1}}{2\cdot 2\cdot 4\cdot 5}$$

$$A_{-4,2} = -\frac{1}{4\cdot 5} + \frac{c_{-1}^2 + c_{-2}^2 + c_{-3}^2 + c_{-4}^2 + c_{-1}c_{-2} + c_{-2}c_{-3} + c_{-3}c_{-1} + c_{-1}c_{-4} + c_{-2}c_{-4} + c_{-3}c_{-4}}{2\cdot 2\cdot 5\cdot 6}$$

(C) We will now obtain the coefficients $A_{n,3}$ by putting $r = 2$ in (45). We get

$$(n + 3)\,A_{n,3} - n\,A_{n-1,3} + \frac{1}{4(n+1)}A_{n+1,1} = \frac{c_n}{2}A_{n,2} \quad \ldots \quad (49)$$

for $n \geqslant 1$ and

$$6\,A_{0,3} - \tfrac{1}{2}A_{-1,1} + \tfrac{1}{2}A_{1,1} = 0$$

(i) From (49), we get

$$A_{0,3} = -\frac{c_1 + c_{-1}}{48}$$

(ii) Putting $n = 1, 2, 3$ in (49) successively, we get

$$A_{1,3} = \frac{1}{192}\{c_1^3 - (c_{-1} + 5\,c_1 + c_2)\}$$

$$A_{2,3} = \frac{1}{480}\{(c_1^3 + c_2^3 + c_1^2c_2 + c_1c_2^2) - (c_{-1} + 6c_1 + 6c_2 + c_3)\}$$

$$A_{3,3} = \frac{1}{960}\{(c_1^3 + c_2^3 + c_3^3 + c_1^2c_2 + c_1c_2^2 + c_2^2c_3 + c_2c_3^2 + c_3^2c_1 + c_3c_1^2 + c_1c_2c_3) - (c_{-1} + 7c_1 + 7c_2 + 7c_3 + c_4)\}$$

$$A_{4,3} = \frac{1}{1680}\{(c_1^3 + c_2^3 + c_3^3 + c_4^3 + c_1^2c_2 + c_1c_2^2 + c_1^2c_3 + c_1c_3^2 + c_1^2c_4 + c_1c_4^2 + c_2^2c_3 + c_2c_3^2 + c_2^2c_4 + c_2c_4^2 + c_3^2c_4 + c_3c_4^2 + c_1c_2c_3 + c_1c_2c_4 + c_4c_1c_3 + c_4c_2c_3) - (c_{-1} + 8c_1 + 8c_2 + 8c_3 + 8c_4 + c_5)\}.$$

The coefficients $A_{-1,3}$, $A_{-2,3}$, $A_{-3,3}$ and $A_{-4,3}$ are obtained from the above by changing c_n to c_{-n} and $A_{n,r}$ to $(-)^n A_{-n,r}$.

(D) To calculate the coefficients $A_{n,4}$, we put $r = 3$ in (45) and get

$$(n+4)A_{n,4} - nA_{n-1,4} + \frac{1}{4(n+1)}A_{n+1,2} = \frac{c_n}{2}A_{n,3} \quad \ldots \quad (50)$$

for $n \geqslant 1$ and

$$8A_{0,4} - \tfrac{1}{2}A_{-1,2} + \tfrac{1}{2}A_{1,2} = 0$$

Following the same procedure as in the above we get

$$A_{0,4} = -\frac{1}{384}(c_1^2 + c_{-1}^2) + \frac{1}{64}$$

$$A_{1,4} = \frac{1}{1920}\{c_1^4 - (c_{-1}^2 + 7c_1^2 + c_2^2 + 2c_1c_2 + c_1c_{-1})\} + \frac{1}{192}$$

$$A_{2,4} = \frac{1}{5760}\{(c_1^4 + c_2^4 + c_1^3c_2 + c_1c_2^3 + c_1^2c_2^2) - (c_{-1}^2 + 8c_1^2 + 8c_2^2 + c_3^2 + 9c_1c_2 + c_1c_{-1} + c_1c_3 + 2c_2c_3 + c_2c_{-1})\} + \frac{1}{384}$$

$$A_{3,4} = \frac{1}{13440}\{(c_1^4 + c_2^4 + c_3^4 + c_1^2c_2^2 + - - + c_1^3c_2 + - - + c_1c_2c_3^2 + - -) - (c_{-1}^2 + 9c_1^2 + 9c_2^2 + 9c_3^2 + c_4^2 + 10c_1c_2 + 10c_2c_3 + 9c_1c_3 + c_1c_{-1} + c_2c_{-1} + c_1c_4 + c_2c_4 + 2c_3c_4 + c_3c_{-1})\} + \frac{1}{640}$$

Similarly we have found

$$A_{0,5} = \frac{1}{3840}\{-(c_1^3 + c_{-1}^3) + 6c_1 + 6c_{-1} + c_{-2} + c_2\}$$

$$A_{0,6} = \frac{1}{46080} \times \{-(c_1^4 + c_{-1}^4) + (8c_1^2 + 8c_{-1}^2 + c_2^2 + c_{-2}^2 + 2c_1c_2 + 2c_{-1}c_{-2} + 2c_1c_{-1})\} - \frac{1}{2304}$$

So we can write the following series for Ψ's.

$$\Psi_0 = 1 - \frac{x^2}{4} - \frac{1}{48}(c_1 + c_{-1})x^3 + \frac{1}{64}\left(1 - \frac{c_1^2 + c_{-1}^2}{6}\right)x^4 + \frac{1}{3840}\{-(c_1^3 + c_{-1}^3) + 6c_1 + 6c_{-1} + c_{-2} + c_2\}x^5 + \frac{x^6}{2304}\left\{-1 - \frac{c_1^4 + c_{-1}^4}{20} + \frac{8c_1^2 + 8c_{-1}^2 + c_2^2 + c_{-2}^2 + 2c_1c_2 + 2c_{-1}c_{-2} + 2c_1c_{-1}}{20}\right\} + - - -$$

$$\Psi_1 = \frac{x}{2}\left[1 + \frac{c_1}{4}x + \frac{1}{8}\left(\frac{c_1^2}{3} - 1\right)x^2 + \frac{1}{192}(c_1^3 - c_{-1} - 5c_1 - c_2)x^3 + \frac{1}{1920}(c_1^4 - \{c_{-1}^2 + 7c_1^2 + c_2^2 + 2c_1c_2 + c_1c_{-1}\} + 10)x^4 + - -\right]$$

$$\Psi_{-1} = -\frac{x}{2}\left[1 + \frac{c_{-1}}{4}x + \frac{1}{8}\left(\frac{c_{-1}^2}{3} - 1\right)x^2 + \frac{1}{192}(c_{-1}^3 - c_1 - 5c_{-1} - c_{-2})x^3 + \frac{1}{1920}(c_{-1}^4 - \{c_1^2 + 7c_{-1}^2 + c_{-2}^2 + 2c_{-1}c_{-2} + c_{-1}c_1\} + 10)x^4 + - -\right]$$

$$\Psi_2 = \frac{x^2}{8}\left\{1 + \frac{c_1 + c_2}{6}x + \frac{1}{12}\left(-1 + \frac{c_1^2 + c_1c_2 + c_2^2}{4}\right)x^2 + - -\right\} \quad .. \quad (51)$$

$$\Psi_{-2} = \frac{x^2}{8}\left\{1 + \frac{c_{-1} + c_{-2}}{6}x + \frac{1}{12}\left(-1 + \frac{c_{-1}^2 + c_{-1}c_{-2} + c_{-2}^2}{4}\right)x^2 + - -\right\}$$

$$\Psi_3 = \frac{x^3}{48}\left\{1 + \frac{c_1 + c_2 + c_3}{8}x + - -\right\}$$

$$\Psi_{-3} = -\frac{x^3}{48}\left\{1 + \frac{c_{-1} + c_{-2} + c_{-3}}{8}x + - -\right\}$$

We will now apply these calculations to obtain the intensity expressions in the theory of the phenomenon we are concerned.

6. *Applications of the above Calculations to the Theory of the Phenomenon.*

In the problem we are concerned, x has to be written as ξ and c's will have the following special values as given by (32).

$$\left.\begin{aligned} c_1 &= i(\rho - 2a\sin\phi); \quad c_{-1} = i(\rho + 2a\sin\phi) \\ c_2 &= 4i(\rho - a\sin\phi); \quad c_{-2} = 4i(\rho + a\sin\phi) \\ c_3 &= 3i(3\rho - 2a\sin\phi); \quad c_{-3} = 3i(3\rho + 2a\sin\phi) \end{aligned}\right\} \quad .. \quad (52)$$

where

$$\rho = \frac{\lambda^2\cos^2\phi}{\mu_0\mu\,\lambda^{*2}}$$

and

$$a = \frac{\lambda}{\mu\,\lambda^*}.$$

Let us write $a \sin\phi$ as $\alpha\rho$. Then

$$\alpha = \frac{\mu_0\,\lambda^*}{\lambda}\tan\phi \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \quad (53)$$

Thus

$$\left.\begin{aligned} c_1 &= i\rho\,(1-2\alpha)\,; \quad c_{-1} = i\rho\,(1+2\alpha) \\ c_2 &= 4i\rho\,(1-\alpha)\,; \quad c_{-2} = 4i\rho\,(1+\alpha) \\ c_3 &= 3i\rho\,(3-2\alpha)\,; \quad c_{-3} = 3i\rho\,(3+2\alpha) \end{aligned}\right\} \qquad .. \qquad .. \quad (54)$$

Substituting the above values of c's in (51), we get for the amplitude functions

$$\Psi_0 = 1 - \frac{\xi^2}{4} - \frac{i\rho}{24}\xi^3 + \frac{1}{64}\left[1 + \frac{(1+4\alpha^2)\,\rho^2}{3}\right]\xi^4 + \frac{i}{1920}\{10\rho + \rho^3(1+12\alpha^2)\}\xi^5 - \left\{\frac{1}{2304} + \frac{\rho^2(11+20\alpha^2)}{7680} + \frac{\rho^4(1+24\alpha^2+16\alpha^4)}{23040}\right\}\xi^6 + - - -$$

$$\Psi_1 = \frac{\xi}{2}\left[1 + \frac{i\rho\,(1-2\alpha)}{4}\xi - \frac{\xi^2}{8}\left(1 + \frac{\rho^2(1-2\alpha)^2}{3}\right) + \frac{i\,\xi^3}{192}\{-\rho^3(1-2\alpha)^3 - 10\rho + 12\alpha\rho\} + \xi^4\left\{\frac{\rho^4(1-2\alpha)^4}{1920} + \frac{\rho^2(33-80\alpha+60\alpha^2)}{1920} + \frac{1}{192}\right\} + - - -\right]$$

$$\Psi_{-1} = -\frac{\xi}{2}\left[1 + \frac{i\rho\,(1+2\alpha)}{4}\xi - \frac{\xi^2}{8}\left(1 + \frac{\rho^2(1+2\alpha)^2}{3}\right) + \frac{i\xi^3}{192}\{-\rho^3(1+2\alpha)^3 - 10\rho - 12\alpha\rho\} + \xi^4\left\{\frac{\rho^4(1+2\alpha)^4}{1920} + \frac{\rho^2(33+80\alpha+60\alpha^2)}{1920} + \frac{1}{192}\right\} + - - -\right] \qquad .. \quad (55)$$

$$\Psi_2 = \frac{\xi^2}{8}\left[1 + \frac{i\rho\,(5-6\alpha)}{6}\xi - \frac{1}{12}\left(1 + \frac{\rho^2(21-48\alpha+28\alpha^2)}{4}\right)\xi^2 + - -\right]$$

$$\Psi_{-2} = \frac{\xi^2}{8}\left[1 + \frac{i\rho\,(5+6\alpha)}{6}\xi - \frac{1}{12}\left(1 + \frac{\rho^2(21+48\alpha+28\alpha^2)}{4}\right)\xi^2 + - -\right]$$

The relative intensity expressions for the various diffraction orders can be

found by finding the series for $\Psi_r \Psi_r\dagger$ where † denotes the conjugate expression. Let the intensity of the rth order be denoted by I_r. Then

$$I_0 = |\Psi_0|^2 = 1 - \frac{\xi^2}{2} + \frac{\xi^4}{32}\left(3 + \frac{\rho^2(1+4a^2)}{3}\right) - \xi^6\left[\frac{5}{576} + \frac{\rho^4(1+24a^2+16a^4)}{11520} + \frac{7\rho^2}{1280} + \frac{\rho^2 a^2}{64} - \frac{\rho^2}{576}\right] + - - -$$

$$I_1 = |\Psi_1|^2 = \frac{\xi^2}{4} - \frac{\xi^4}{16}\left[1 + \frac{\rho^2(1-2a)^2}{12}\right] + \frac{\xi^6}{192}\left[\frac{5}{4} + \frac{\rho^2(9-20a+20a^2)}{10} + \frac{\rho^4(1-2a)^4}{120}\right] + - -$$

$$I_{-1} = |\Psi_{-1}|^2 = \frac{\xi^2}{4} - \frac{\xi^4}{16}\left[1 + \frac{\rho^2(1+2a)^2}{12}\right] + \frac{\xi^6}{192}\left[\frac{5}{4} + \frac{\rho^2(9+20a+20a^2)}{10} + \frac{\rho^4(1+2a)^4}{120}\right] + - - \qquad (56)$$

$$I_2 = \frac{\xi^4}{64} - \frac{\xi^6}{384}\left[1 + \frac{\rho^2}{12}(12a^2 - 24a + 13)\right] + - - -$$

$$I_{-2} = \frac{\xi^4}{64} - \frac{\xi^6}{384}\left[1 + \frac{\rho^2}{12}(12a^2 + 24a + 13)\right] + - - -$$

$$I_3 = \frac{\xi^6}{2304} + - - -$$

One can now clearly see the asymmetry between I_1, and I_{-1} and I_2 and I_{-2}. The asymmetry between I_3 and I_{-3} consists in the higher terms than the one term written.†

7. *Discussion of Experimental Data.*

(*a*) *The case when ρ is negligible and a is zero.*—The various I's are the squares of the Bessel functions if $\rho = 0$. This case corresponds to that treated in Part I. Thus the restrictions in Part I amount to ρ being small. This could be so when the wave-length of sound is so large that ρ becomes a magnitude which has not much influence in the intensity expressions. This case has been achieved experimentally by Bär who finds perfect quantitative agreement with the theory.

(*b*) *The case when ρ is not negligible.*—When a is not zero (*i.e.*, oblique incidence) the theory shows that there will be no symmetry in the diffraction pattern, *i.e.*, the intensity of the rth order will not be equal to that of the $-r$th order. This fact is in agreement wit the experimental results of Debye and Sears, Lucas and Biquard, Bär and Parthasarathy.

† One may also verify from the above that
$I_0 + I_1 + I_{-1} + I_2 + I_{-2} + I_3 + I_{-3} + - - = 1.$

Parthasarathy has found that in the case of oblique incidence the intensity is distributed more towards that side which favours the 'reflection' of the incident light if the sound waves had acted as mirrors. Theoretically the expressions obtained in (56) seem to show that this would be so if we restrict our attention to the *first two terms* in each of the intensity expressions. If we make such a restriction, the expressions (56) show that the intensity of any positive order is greater than the corresponding negative order. The positive orders are situated towards that side which favour reflection of the incident light if the supersonic waves had acted as mirrors. However, it is certainly very necessary to carry our calculations of the intensity expressions for a greater number of terms and then alone we can definitely say which side would be more intense under any definite experimental conditions.

Recently, Parthasarathy made an investigation of the diffraction phenomenon by keeping all the parameters constant except the angle of incidence of light to the sound waves which he changed continuously. He has recorded that the first order attains its maximum intensity when the incident angle to the sound waves corresponds nearly to the Bragg reflection angle which is $\lambda/2\lambda^*$. Similarly he has recorded that the intensity of the second order attains its maximum when the incident angle is about λ/λ^*. If we restrict our attention *to the first two terms* of the intensity expressions (56), it is easy to see that the first order would attain maximum intensity when $a = \frac{1}{2}$ or $\phi = \lambda/2\mu_0\lambda^*$. Also it can be seen that the second order attains its maximum intensity when $\phi = \lambda/\mu_0\lambda^*$. It is to be remembered that μ_0 is the refractive index of the medium. If the path of the incident light is not normal to the face of the cell, then the maximum intensity of the first order will appear when the angle between the path of the incident light (which travels in air) and the sound wave-fronts is $\lambda/2\lambda^*$ and the maximum intensity for the second order will appear when the angle between the path of the incident light and the sound waves is λ/λ^*.

It may seem certainly very necessary to further the calculations of the intensity expressions to higher terms and see whether there are actually maxima of the intensity of the various orders at definite angles as is claimed. *The intensity expression obtained here for the first order itself shows that it may be so.* If however the first order would attain maximum intensity at a definite angle independent of the other parameters ξ and ρ, then there should be a solution for the equation $\frac{dI_1}{da} = 0$ independent of ξ and ρ. If $\frac{dI_1}{da} = 0$,*

* ρ has the factor $\text{Cos}^2\,\phi$ and so it depends on ϕ. But if ϕ is to vary in a small range, the dependence can be ignored. ϕ is really very small in experiments.

$$-\frac{\xi^4\rho^2}{16\times 12}\,2\,(1-2a)\times -2+\frac{\xi^6}{4}\left\{\frac{4\rho^4(1-2a)^3\times -2}{5760}\right.$$

$$\left.+\frac{\rho^2(-20+40a)}{480}\right\}+--=0 \qquad .. \quad (57)$$

Equating the coefficients of the independent terms to 0 we get

$$a=\tfrac{1}{2}$$

or $$\phi=\lambda/2\mu_0\lambda^* \qquad .. \quad .. \quad .. \quad .. \quad .. \quad (58)$$

The condition $\frac{dI_1}{da}=0$ is only a necessary condition for the occurrence of the maximum. We should then see for a maximum that $\frac{d^2I_1}{da^2}$ is less than zero. These considerations point out that the maximum of the first order may appear when $a=\frac{1}{2}$, possibly under some conditions.

If we consider only the first two terms for the intensity expression of I_2, it can be seen that I_2 becomes maximum when

$$a=1$$

or $$\phi=\lambda/\mu_0\lambda^* \qquad .. \quad .. \quad .. \quad .. \quad .. \quad (59)$$

We are fully aware that the further development of the intensity expressions is greatly needed to interpret the experimental results, but the series method which has been tried here to evaluate them leads to the following result in the theory. *This work seems to clearly show that the maxima of the orders may appear at unique angles, possibly under some conditions.*

8. Expressions for Amplitudes in the Case of Normal Incidence.

If we put $a=0$, in the fourth section, we can obtain the series for the amplitude functions in the case of normal incidence. But we have worked out this case separately and we give in the following our final results without giving the details of calculation as they are similar to those in the case of oblique incidence.

$$\Psi_0=1-\frac{\xi^2}{4}-\frac{i\rho\xi^3}{24}+\frac{1}{64}\left(1+\frac{\rho^2}{3}\right)\xi^4$$

$$+\frac{i\rho}{192}\left(1+\frac{\rho^2}{10}\right)\xi^5-\left(\frac{\rho^4}{23040}+\frac{11\rho^2}{7680}+\frac{1}{2304}\right)\xi^6$$

$$-i\left(\frac{\rho^5}{322560}+\frac{\rho^3}{2688}+\frac{\rho}{4608}\right)\xi^7$$

$$+\left(\frac{\rho^6}{5160960}+\frac{463\rho^4}{5160960}+\frac{17\rho^2}{184320}+\frac{1}{147456}\right)\xi^8+--$$

$$\Psi_1 = \frac{\xi}{2}\Big[1 + \frac{i\rho}{4}\,\xi - \frac{1}{24}\,(\rho^2+3)\,\xi^2 - \frac{i\rho}{192}\,(\rho^2+10)\,\xi^3 + \Big(\frac{\rho^4}{1920} + \frac{11\rho^2}{640} + \frac{1}{192}\Big)\xi^4 + i\Big(\frac{\rho^5}{23040} + \frac{\rho^3}{192} + \frac{7\rho}{2304}\Big)\xi^5 - \Big(\frac{\rho^6}{322560} + \frac{463\rho^4}{322560} + \frac{17\rho^2}{11520} + \frac{1}{9216}\Big)\xi^6 - i\Big(\frac{\rho^7}{5160960} + \frac{61\rho^5}{172032} + \frac{901\rho^3}{1290240} + \frac{\rho}{12288}\Big)\xi^7 + \Big(\frac{\rho^8}{92897280} + \frac{2431\rho^6}{30965760} + \frac{14779\rho^4}{46448640} + \frac{115\rho^2}{2211840} + \frac{1}{737280}\Big)\xi^8 + - -\Big]$$

$$\Psi_2 = \frac{\xi^2}{8}\Big[1 + \frac{5i\rho}{6}\,\xi - \tfrac{1}{4}\Big(\frac{7\rho^2}{4} + \tfrac{1}{3}\Big)\xi^2 - i\Big(\frac{17\rho^3}{96} + \frac{\rho}{12}\Big)\xi^3 + \frac{341\rho^4}{5760} + \frac{17\rho^2}{288} + \frac{1}{384}\Big)\xi^4 + i\Big(\frac{13\rho^5}{768} + \frac{361\rho^3}{10080} + \frac{7\rho}{2304}\Big)\xi^5 - \Big(\frac{5461\rho^6}{1290240} + \frac{6257\rho^4}{322560} + \frac{247\rho^2}{92160} + \frac{1}{23040}\Big)\xi^6 - - -\Big]$$

$$\Psi_3 = \frac{\xi^3}{48}\Big[1 + \frac{7i\rho}{4}\,\xi - \frac{1}{80}\,(147\rho^2+5)\,\xi^2 - i\Big(\frac{22}{15}\,\rho^3 + \frac{23\rho}{192}\Big)\xi^3 + \Big(\frac{1859\rho^4}{1920} + \frac{143\rho^2}{960} + \frac{1}{640}\Big)\xi^4 + i\Big(\frac{2821\rho^5}{5120} + \frac{5391\rho^3}{35840} + \frac{5\rho}{1536}\Big)\xi^5 + - -\Big]$$

$$\Psi_4 = \frac{\xi^4}{384}\Big[1 + 3i\rho\xi - \Big(\frac{209\rho^2}{40} + \frac{1}{20}\Big)\xi^2 - i\Big(\frac{143\rho^3}{21} + \frac{19\rho}{20}\Big)\xi^3 + \Big(\frac{65351\rho^4}{8960} + \frac{71\rho^2}{448} + \frac{1}{960}\Big)\xi^4 + i\Big(\frac{108511\rho^5}{16128} + \frac{40499\rho^3}{120960} + \frac{\rho}{288}\Big)\xi^5 + - -\Big] \qquad (60)$$

$$\Psi_5 = \frac{\xi^5}{3840}\Big[1 + \frac{55i\rho\xi}{12} - \Big(\frac{143\rho^2}{12} + \frac{1}{24}\Big)\xi^2 - i\Big(\frac{30745\rho^3}{1344} + \frac{19\rho}{96}\Big)\xi^3 + \Big(\frac{174889\rho^4}{24192} + \frac{11419\rho^2}{24192} + \frac{1}{1344}\Big)\xi^4 + - -\Big]$$

$$\Psi_6 = \frac{\xi^6}{46080}\Big[1 + \frac{13i\rho\xi}{2} - \Big(\frac{2639\rho^2}{112} + \frac{1}{28}\Big)\xi^2 - i\Big(\frac{125749\rho^3}{2016} + \frac{5\rho}{21}\Big)\xi^3 + \Big(\frac{125749\rho^4}{1120} + \frac{34768\rho^2}{40320} + \frac{1}{1792}\Big)\xi^4 + - -\Big]$$

$$\Psi_7 = \frac{\xi^7}{645120}\left[1 + \frac{35i\rho\xi}{4} - \left(\frac{6069\rho^2}{144} + \frac{1}{32}\right)\xi^2 + - -\right]$$

The above series for the Ψ's are rather slowly convergent and it is rather difficult to find their values for any pair of values ρ and ξ.

If we put $\rho = 0$ in the above, the series then represent the well-known expansions of the Bessel Functions. In this exterme case we can determine the relative values of the amplitudes simply as a function of ξ. But when ρ is not zero the calculation is not simple. If we know μ, the amplitude of the fluctuation of the refractive index, we can determine the values of ξ and ρ by the following relations

$$\xi = \frac{2\pi\mu Z}{\lambda},$$

$$\rho = \frac{\lambda^2}{\mu_0\mu\,\lambda^{*2}}.$$

Only when the series given above converge rapidly for determined ξ and ρ, they will be of use for practical work.

9. *A Possible Method of Determining the Amplitude of the Fluctuation of the Refractive Index at High Supersonic Frequencies.*

The method outlined in the following is an indirect one and applicable only under heavy restrictions.

(1) The supersonic frequency should be high.

(2) The length of the cell should be decreased to such an extent that there should be good reason to believe that $\frac{2\pi\mu L}{\lambda}$ is small.

The diffraction pattern in the case of normal incidence has to be studied first and the relative intensity of the central order to the first (or *minus* first) order is to be determined. Let it be Δ_1. Then the cell has to be rotated to such an extent that the first order attains its maximum intensity. Experimental conditions ought to be such that the obliquity will be nearly $\lambda/2\lambda^*$. Let now the ratio of the first order to the *minus* first order be Δ_2. If L denotes the length of the cell, $\xi = \frac{2\pi\mu L}{\lambda}$. Then

$$\frac{1 - \frac{\xi^2}{2} + \frac{\xi^4}{32}\left(3 + \frac{\rho^2}{3}\right) - -}{\frac{\xi^2}{4} - \frac{\xi^4}{16}\left[1 + \frac{\rho^2}{12}\right] - -} = \Delta_1$$

$$\frac{\frac{\xi^2}{4} - \frac{\xi^4}{16} + - -}{\frac{\xi^2}{4} - \frac{\xi^4}{16}\left(1 + \frac{\rho^2}{3}\right)} = \Delta_2 \qquad .. \quad .. \quad .. \quad (61)$$

Since $\rho\xi = 2\pi\lambda L/\mu_0 \lambda^{*2}$, the vaules of ρ and ξ can be determined by each of the above equations. First of all the two sets of values are to be consistent. If so, one can then determine μ, the amplitude of the fluctuation of the refractive index by knowing the formulæ for ρ and ξ.

The restrictions in the above method are *rather very heavy* so that it may be difficult to arrange the experimental conditions in the required manner. The method also depends on the assumption that the *supersonic wave in the medium is a simple harmonic one. Therefore the above is only offered as a suggestion to be tested out experimentally.*

10. Summary.

A general review of the theory of the diffraction of light by high frequency sound waves developed in these *Proceedings* by Raman and Nath is presented. The solution of the difference—differential equation due to them given in Parts IV and V of their papers is attempted here by the series method. The results obtained in this paper offer an explanation for the experimental results due to Bär and Parthasarathy who have studied the phenomenon at oblique incidence of light to the sound waves. That the idea of 'propagation' of light in a quasi-homogeneous medium is fundamental and preferable to the undefined idea 'reflection' in such a medium, is pointed out.

The author is grateful to Professor C. V. Raman for many discussions they had since the theory was initiated by them.

Note added in proof.

A report of an interesting investigation of the theory of this phenomenon by Wannier and Estermann of Geneva based on the partial differential equation governing the propagation of light in a quasi-homogeneous medium has appeared in the recent issue of *Helvetica Physica Acta*. If we write the Fourier expansion for $f(\alpha, z)$ in Brillouin's pamphlet (equation 48) or if we write $\Sigma f_r(k_r) \exp(ik_r z)$ for f_r in Raman-Naths' paper, (Part IV) equation 9, we get the equation obtained by Wannier and Estermann. The comparison of their calculated results for $\Theta = 1$ with those of Raman and Nath in their *preliminary theory* requires however a justification. Bär has definitely found experimentally the region of the perfect quantitative applicability of the preliminary theory. One can however calculate ρ and ξ of this paper on Wannier-Estermann's choice of special experimental conditions and substitute them in the expressions (56) obtained in this paper, and find the region of the applicability of the preliminary theory for Wannier-Estermann's choice of the experimental conditions. Even if the length of the cell is not negligible but if the wave-length of sound is large (10^{-1} cm.), the preliminary theory will be applicable as has been experimentally established by Bär.

STUDIES IN ATMOSPHERIC RADIATION.

A Discussion of Some Observations of Nocturnal Radiation made at Poona and Sinhagad.

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The variation in the amount of heat radiation received from the clear atmosphere during the course of the night has been studied by Angstrom,[1] Boutaric[2] and Kimball.[3] They find that in general there is a decrease of atmospheric radiation after sunset and that the radiation attains a minimum value a little before sunrise. In attempting to find whether there is any effect on atmospheric radiation which could be traced to changes in the amount of ozone which is known to be always present in the upper atmosphere or to changes in its temperature, Angstrom corrected the measured values of atmospheric radiation for changes of temperature and humidity in the lower layers and found that there was a maximum of radiation some 2 or 3 hrs. after mid-night.

In a recent paper, Ramanathan and Ramdas[4] have discussed the question of the dependence of atmospheric radiation on clear nights on the temperature and moisture content of the lower layers of the atmosphere. By dividing the spectrum of the temperature radiation of water vapour of the atmosphere into three groups of wave-lengths, the energy in the three groups being S_1, S_2 and S_3 where S_1 relates to the region in which the decimal absorption co-efficient a is less than 1 ($8 \cdot 5$–$10 \cdot 5\ \mu$ and $3 \cdot 5$–$4 \cdot 3\ \mu$), S_2 to the region where a lies between 1 and 10 and S_3 to the region where a exceeds 10 ($5 \cdot 1$–$7 \cdot 9\ \mu$ and $> 15 \cdot 3\ \mu$), they have shown that the water-vapour radiation can be expressed in the form

$$S = S_3 + S_2 - S_2 \exp\ (-\tfrac{3}{2}\ k_2\, w)$$

which is similar in form to Angstrom's formula for atmospheric radiation,

$$S/\sigma T^4 = A - B.\ 10^{-\gamma e}$$

where A, B and γ are constants, e and T are the vapour pressure and temperature respectively of the air near the instrument and σ is Stefan's constant.

The two expressions are equivalent when the total precipitable water in the atmosphere is expressed as a linear function of the vapour pressure at the surface.

During radiation (clear and calm) nights, considerable cooling takes place near the surface of the ground. This should cause an appreciable effect on the temperature radiation depending on the S_3 part, but little on the S_2 fraction as the latter would come from a large thickness of the atmosphere.

The present experiments were primarily made for determining the march of radiation-loss from a horizontal surface and of the atmospheric radiation received on such a surface during the course of the night and to see how far the observations could be explained by changes in temperature and humidity of the lower layers.

The observations were carried out during some clear nights in February and March 1935 at three places, *viz.*, (1) the Agricultural Meteorological Observatory at Poona, (2) the top of the tower of the Poona Meteorological Office, and (3) the top of Sinhagad, a hill 4,300 ft. above sea-level and about 15 miles to the south-west of Poona. The horizontal distance between the first two places is about 1,300 yds. and the height of the tower of the Meteorological Office above the level of the Agricultural Meteorological Observatory is 120 ft. Some of the observations were simultaneous.

Observations at Poona.

For the measurement of nocturnal radiation, two Angstrom pyrgeometers were used. Their constants were determined in the laboratory and they were also compared with each other by simultaneous observations of sky radiation at the same place. The inter-comparisons showed that the results given by the two instruments differed from each other by less than half per cent.

Observations throughout the night were made at the Agricultural Meteorological Observatory on 5 days and at the Meteorological Office Tower on 9 days. On two of these nights, the observations were simultaneous, and they are summarised in Table I; those on the 27th February 1935 are

TABLE I.

Agricultural College							Meteorological Office Tower						
Time hrs.	Temperatue °C.		Vapour Pressure	Net Radiation	S	$S/\sigma T^4$	Time hrs.	Temperature °C.		Vapour Pressure	Net Radiation	S	$S/\sigma T^4$
	T_d	T_w	mm.	Cal./cm.² min.	Cal./cm.² min.			T_d	T_w	mm.	Cal./cm.² min.	Cal./cm.² min.	
							27-2-1935						
2145	25·2	14·3	6·8	·197	·450	·696	2130	25·5	14·7	7·1	·201	·449	·691
2200	24·8	14·5	7·2	·197	·446	·694	2200	25·0	14·5	7·1	·198	·447	·693
2300	23·8	13·5	6·5	·194	·441	·694	2300	24·4	14·0	6·8	·195	·445	·695
2400	23·5	13·0	6·0	·190	·442	·699	2400	24·0	13·5	6·4	·187	·450	·706
0100	22·0	12·7	6·4	·187	·432	·698	0105	22·5	12·5	5·9	·186	·438	·702
0300	18·3	11·0	6·2	·164	·425	·722	0300	20·0	12·5	7·1	·173	·430	·713
0405	14·1	8·0	5·0	·151	·405	·728	0430	18·5	12·0	7·3	·173	·415	·706
0500	13·8	9·5	6·8	·148	·406	·733	0500	18·5	12·0	7·3	·180	·411	·695
0600	13·0	8·9	6·5	·144	·403	·737	0600	18·0	12·0	7·5	·169	·418	·714
							28-2-1935						
1930	25·3	14·3	6·7	·189	·459	·708	1920	25·8	14·5	6·7	·193	·460	·704
2040	23·0	13·5	6·9	·183	·445	·709	2020	24·2	14·2	7·1	·189	·449	·704
2130	22·8	12·8	6·1	·192	·434	·693	2130	23·0	13·0	6·2	·194	·434	·691
2230	22·3	12·3	5·7	·197	·425	·683	2230	22·5	12·5	5·9	·196	·424	·684
2400	21·8	11·8	5·4	·190	·428	·693	2400	21·5	12·0	5·8	·193	·422	·686
0100	20·5	11·0	5·1	·187	·420	·692	0100	20·9	12·0	6·1	·189	·421	·690
0300	19·7	10·4	4·8	·185	·415	·692	0230	20·6	11·5	5·9	·178	·418	·701
0400	17·1	9·0	4·6	·166	·413	·714	0400	19·5	11·0	5·6	·179	·416	·700
0500	15·0	9·0	5·6	·155	·408	·725	0530	17·8	11·0	6·4	·165	·414	·715
0600	13·0	8·0	5·5	·144	·403	·737	0600	17·5	10·5	6·0	·168	·411	·713
0620	12·9	7·9	5·5	·139	·407	·745	0630	17·5	10·5	6·0	·163	·416	·718

given in Fig. 1. T_d and T_w in these tables denote dry and wet bulb temperatures respectively.

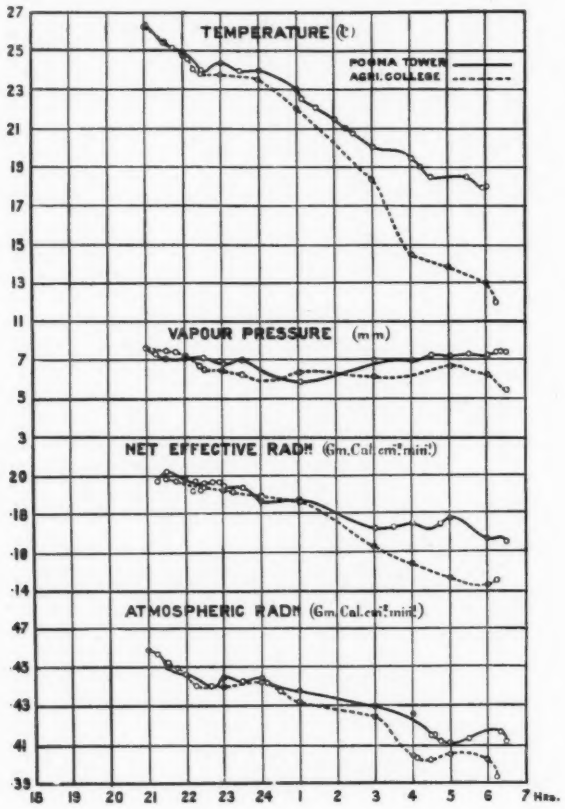

FIG. 1.

These observations show that—

(1) on clear nights, in settled weather, both the net radiation as well as the radiation from the atmosphere decrease with time after sunset, becoming a minimum at about the time of minimum temperature;

(2) both these quantities, especially the net radiation, show a greater fall at the ground observatory than at the tower; and

(3) the decrease of atmospheric radiation during a single night depends more on the fall of temperature of the air layers nearest to the instrument than on the change of vapour pressure. The ratio $S/\sigma T^4$ has

TABLE II.

Meterological Office Tower							Sinhagad						
Time hrs.	Temperature °C.		Vapour Pressure	Net Radiation	S	$S/\sigma T^4$	Time hrs.	Temperature °C.		Vapour Pressure	Net Radiation	S	$S/\sigma T^4$
	T_d	T_w	mm.	Cal./cm.² min.	Cal./cm.² min.			T_d	T_w	mm.	Cal./cm.² min.	Cal./cm.² min.	
							9-3-1935						
2000	27·3	11·2	1·9	·226	·439	·660	2000	22·8	7·0	0·0	·261	·365	·583
2100	26·2	11·0	2·2	·242	·414	·631	2100	21·9	7·2	0·3	·256	·363	·586
2200	24·0	10·5	2·8	·234	·403	·633	2200	21·6	7·2	0·4	·258	·358	·581
2300	24·0	10·5	2·8	·266	·410	·645	2300	21·3	7·0	0·4	·252	·362	·589
2400	23·0	10·5	3·3	·214	·414	·659	2400	20·9	7·0	0·6	·258	·352	·577
0200	21·2	9·5	3·1	·205	·406	·664	0200	20·4	6·6	0·0	·250	·352	·581
0300	19·0	8·0	2·5	·205	·390	·656	0300	19·5	6·8	1·1	·247	·352	·588
0400	19·0	8·0	2·5	·205	·390	·656	0400	19·4	6·8	1·1	·247	·351	·588
0510	18·0	8·3	3·4	·199	·389	·662	0500	19·2	6·5	0·9	·244	·352	·591
0530	18·0	8·2	3·3	·193	·394	·671	0530	18·6	6·3	1·1	·231	·352	·596
0600	17·5	8·0	3·3	·190	·393	·674	0600	18·2	6·4	1·3	·242	·346	·588
0620	17·5	8·0	3·3	·182	·401	·688	0625	18·7	6·5	1·2	·233	·359	·606
							10-3-1935						
1947	28·6	15·0	6·0	·211	·474	·692	1945	24·0	10·8	3·1	·215	·422	·660
2007	28·5	15·0	6·0	·208	·468	·693	2005	23·9	11·0	3·4	·215	·421	·662
2100	28·0	14·8	6·0	·217	·454	·677	2100	23·7	11·0	3·5	·215	·419	·661
2200	27·2	13·6	4·9	·202	·461	·695	2200	23·0	10·6	3·4	·217	·411	·654
2310	25·0	13·0	5·2	·199	·446	·691	2305	22·6	9·5	2·4	·212	·413	·658
2400	24·5	12·3	4·6	·196	·445	·694	2400	22·2	8·9	1·9	·215	·406	·654
0200	22·5	10·8	3·9	·168	·456	·731	0200	21·0	8·0	1·5	·205	·406	·664
0305	19·0	11·4	6·3	·157	·438	·732	0310	20·6	8·0	1·7	·205	·403	·663
0430	18·0	10·3	5·6	·165	·422	·719	0435	20·4	7·8	1·6	·207	·399	·658
0500	18·0	9·8	5·0	·160	·427	·727	0500	20·0	7·8	1·8	·205	·398	·660
0600	18·0	9·8	5·0	·152	·435	·741	0600	20·1	8·2	2·2	·202	·402	·666
0615	18·0	9·8	5·0	·155	·432	·734	0625	20·0	8·0	2·0	·205	·398	·660

been tabulated in the last column of each table. It will be seen that while in the earlier part of the night the value of this quantity is nearly the same at the two levels, there is a considerable difference between them in the early morning hours, the values at the ground observatory being higher. Neglecting the effect of the change of the vapour pressure near the ground, the figures in the last column indicate that the effective radiating atmosphere at the ground observatory is warmer in the morning than the air near the instrument. This is to be expected from the fact that the nocturnal cooling decreases rapidly

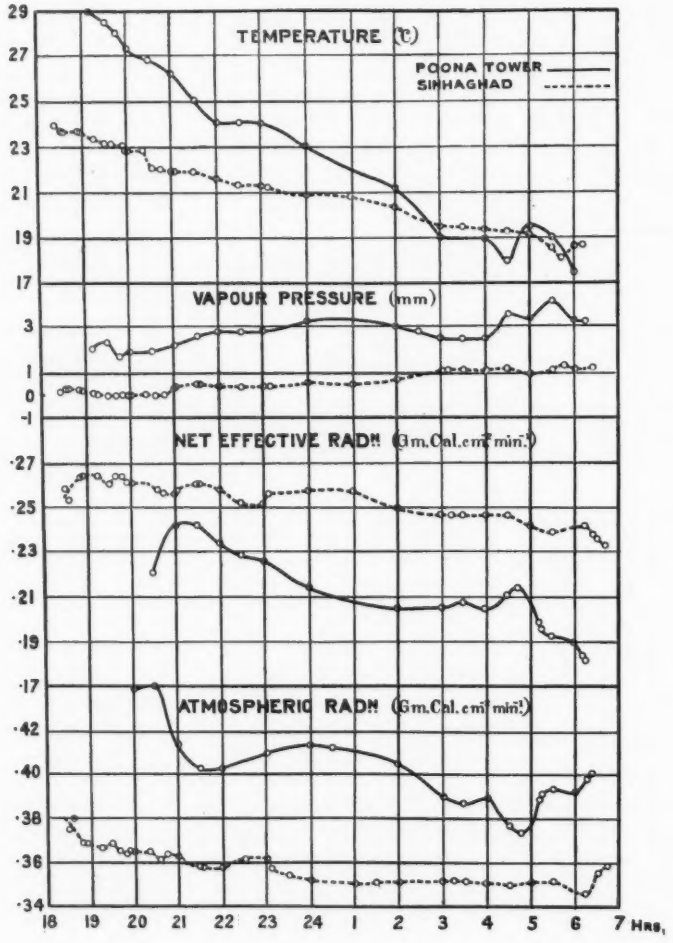

FIG. 2.

with height above ground. At the top of the tower, the difference between the effective radiating temperature of the atmosphere and the actual temperature of the air near the instrument is smaller than at the ground-level.

If this explanation is correct, we should expect even less variation in $S/\sigma T^4$ during the night if we take observations of sky radiation at a sufficiently high level in the atmosphere well above the region of ground cooling. Observations taken at Sinhagad simultaneously with observations at Poona and given in Table II support the above view. The data of 9th March 1935 are also represented diagrammatically in Fig. 2. As is to be expected the variation of temperature at the top of the hill is considerably smaller than on the plain, being only 4° to 5° C. during the night. Correspondingly both the atmospheric radiation and the ratio $S/\sigma T^4$ show smaller variation. The last quantity remains practically constant during the night. It is interesting to note that at the hill also, the atmospheric radiation is much less responsive to changes of vapour pressure than to changes of temperature.

We shall now see whether the increase of $S/\sigma T^4$ at the lower levels during the night can be accounted for if we consider the atmospheric radiation as composed of two parts, (1) the radiation S_3 in the portions of the heat spectrum where the water vapour is highly absorbing and (2) the radiation S_2 $(1-10^{-\gamma e})$ in the spectral regions where water vapour is moderately absorbing $(\alpha > 1 < 10)$. Since S_3 comes from a comparatively thin layer near the ground, where there is considerable cooling during the night, it will undergo marked decrease during the night. The variation in the terms involving S_2 will be much smaller unless there is a significant change of air mass in the upper atmosphere over the place.

In Table III are given the values of atmospheric radiation measured in the evening and the succeeding morning on a number of days. The decrease of atmospheric radiation during the night (Δ S) is given in column 8. The change in black body radiation corresponding to the actual change of temperature near the instrument from evening to the succeeding morning $\Delta(\sigma T^4)$ is given in column 9. The ratio of the change in the sky radiation to that of the radiation from a black body is given in the last column. It will be seen that on the average $\Delta S/\Delta \sigma T^4$ is 0·47, which is about the same as the ratio of S_3 radiation to the total black body radiation at the temperatures experienced during the nights under consideration. The above result suggests that most of the variation in the radiation from the atmosphere which takes place during the course of the night may be attributed to the variation in the S_3 part of the radiation which comes from the air layers near

TABLE III.

Date	Place	T at 21 hrs.	T at 6 hrs.	ΔT	S at 21 hrs.	S at 6 hrs.	ΔS	Δ(σT⁴)	ΔS / Δ(σT⁴)
27-2-35	Ag. Met. Obs.	26·3	13·0	13·3	·459	·403	·056	·110	·51
,,	M. O. Tower	26·3	18·0	8·3	·459	·418	·041	·071	·58
28-2-35	Ag. Met. Obs.	23·0	13·0	10·0	·435	·403	·032	·081	·40
,,	M. O. Tower	23·4	17·5	5·9	·440	·411	·029	·050	·58
9-3-35	M. O. Tower	26·2	17·5	8·7	·414	·393	·021	·076	·27
,,	Sinhagad	21·9	18·6	3·3	·363	·348	·015	·027	·55
10-3-35	M. O. Tower	28·0	18·5	9·5	·463	·435	·028	·079	·34
,,	Sinhagad	23·7	20·1	3·6	·419	·402	·017	·031	·55
12-3-35	M. O. Tower	28·5	17·0	11·5	·437	·397	·040	·099	·40
,,	Sinhagad	24·6	20·5	4·1	·398	·379	·019	·034	·56

the instrument. On some nights, the decrease of the ratio near the ground is much smaller than 0·50. This is due to the fact that the nocturnal cooling is maximum near the ground and decreases with height; when there is a rapid change of temperature with height, the surface temperature of the air cannot be taken as the effective temperature of the radiating layer even for S_a radiation.

We shall now discuss the variation with height of the mean atmospheric radiation during the night at Poona and Sinhagad. From Angstrom's equation

$$S/\sigma T^4 = 0{\cdot}77 - 0{\cdot}28 \times 10^{-0{\cdot}074e}$$

it will be seen that the atmospheric radiation S depends upon T the temperature and e the vapour pressure near the instrument; knowing the mean values of T and e it is easy to calculate $S/\sigma T^4$ at the two levels. In Table IV

TABLE IV.

Date	Mean Temperature °C.		Vapour Pressure mm.		Δe	S/σT⁴		Difference of S/σT⁴ between Poona and Sinhagad	
	Poona Tower	Sinhagad	Poona Tower	Sinhagad		Poona Tower	Sinhagad	Observed	Calculated
9-3-1935	21·2	20·2	2·8	0·8	2·0	·658	·588	·070	·071
10-3-1935	22·9	21·7	5·3	2·4	2·9	·710	·660	·050	·073
12-3-1935	23·5	22·9	3·7	1·8	1·9	·663	·619	·044	·057

are given the mean values of T, e and $S/\sigma T^4$ along with the calculated and observed values of the difference between $S/\sigma T^4$ at Poona and that at Sinhagad. The magnitude of this difference is indicated fairly satisfactorily by Angstrom's formula.*

TABLE V. 9–3–35.

Sinhagad			Meteorological Office Tower, Poona		
Time	Vap. Pr. mm.	R.H. %	Time	Vap. Pr. mm.	R. H. %
1915	0·08	0·3	1910	2·0	7
1930	0·14	0·7	1930	2·3	8
1940	0·29	1·4	1945	1·7	6
2000	0·33	1·6	2000	1·9	7
2035	0·22	1·1	2030	1·9	7
2100	0·3	1	2100	2·2	9
2130	0·5	2	2130	2·6	11
2200	0·4	2	2200	2·8	12
2230	0·4	2	2230	2·8	12
2300	0·4	2	2300	2·8	12
0000	0·6	3	0000	3·3	16
0200	0·6	3	0200	3·1	16
0300	1·1	6	0300	2·5	15
0400	1·1	7	0400	2·5	15
0430	1·2	7	0430	3·6	23
0500	0·9	5	0510	3·4	20
0530	1·1	7	0530	4·2	25
0600	1·2	7	0600	3·3	22

* The mean values of $S/\sigma T^4$ during each night at the Agricultural Meteorological Observatory and at the top of the Meteorological Office Tower are nearly the same; this is to be expected because the total precipitable water in the atmosphere above these places is practically the same and the differences in the mean temperatures are small.

One of the days, *viz.*, the 9th March 1935 was an exceptionally dry day; the variation of vapour pressure and humidity on that night at Sinhagad and Poona are given in Table V. At Poona the vapour pressure varied from 1·7 mm. at 1945 hrs. on the 9th to 4·2 mm. at 0530 hrs. on the 10th, whereas at Sinhagad it was as low as 0·08 mm. at 1915 hrs. on the 9th and increased to 1·1 mm. only at 0530 hrs. on the 10th. The humidity varied at Poona from 7 per cent. to 25 per cent. but at Sinhagad it never rose above 7 per cent. throughout the night after the minimum value of 0·3 per cent. at 1915 hrs.

It is interesting to note, as pointed out in an earlier paper,[5] that in spite of the extraordinarily low value of the vapour pressure on 9th March 1935 at Sinhagad the value of $S/\sigma T^4$ did not fall below 0·58. This suggests that there was sufficient precipitable water vapour in the atmosphere above Sinhagad level to contribute to the S_2 and S_3 radiations received by a horizontal surface.

The uncertainties connected with the measurement of the effective radiative temperature of air and more than all, the difficulty of ascertaining the changes in the moisture content of the atmosphere as a whole during the course of the night make it very difficult to detect the radiation effect (if any) of the ozone in the upper atmosphere.

In conclusion the author desires to express his thanks to the Director-General of Observatories for the facilities given for this investigation and to Dr. K. R. Ramanathan and Dr. L. A. Ramdas for their guidance and encouragement. The author's thanks are also due to Mr. J. V. Karandikar, for his help in taking the observations.

Summary.

The paper discusses the results of measurements of nocturnal heat radiation received from the atmosphere at Poona and Sinhagad. The measurements were carried out in February and March 1935 with Angstrom pyrgeometers. Simultaneous measurements were made at the Agricultural Meteorological Observatory and the top of the tower of the Poona Meteorological Office and also from the latter and the top of Sinhagad, a hill 2,500 ft. above Poona level and distant 15 miles from Poona.

It is shown that on clear nights at all the three places there was a decrease of radiation from the atmosphere after sunset and that the decrease was a maximum at ground-level and minimum at Sinhagad. This decrease expressed as a fraction of the change in black body radiation corresponding to the change of temperature of the air near the instrument was on the average 0·47, but the ratio was smaller at lower levels than at higher. The

results are discussed with reference to Angstrom's formula for atmospheric radiation.

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Erratum

Vol. IV, No. 1, page 132, Table IV, column A, line 8, *for* "0" *read* "27·74" *against* Benzene 1st series and "27·12" *against* 2nd series.